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ON THE PREPARATION OF IRON AND STEEL SPECIMENS FOR MICROSCOPIC INVESTIGATIONS

By Francis F. Lucas

Abstract

A given lens system has certain potential resolving powers. This potential resolving power may or may not be fully realized in practice. Even a low power objective has remarkable resolving ability and the very high aperture objectives are capable of furnishing sharp brilliant images of details measuring about two hundred atom diameters.

The author describes in this paper methods and materials for the critical preparation of iron and steel specimens. A flotation apparatus which he has developed for the preparation of abrasives is described and a typical particle size analysis of a magnesium oxide abrasive prepared by this method is given.

THERE are certain paragraphs from a report[1] presented before the International Congress for Testing Materials held in Zurich Switzerland in 1931 which the writer would like to repeat here as an introduction to the subject of preparing iron and steel specimens for metallographic examination. It was stated:

"In the preparation of metallographic specimens our object is to produce a highly polished plane surface free from alterations so that the details of structure developed by etching will be typical of the metal as a whole. Our aim is not always fully achieved but in most

[1]F. F. Lucas, "Advances in Microscopy", *Proceedings Zurich Congress*, International Association for Testing Materials, September 1931.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The author, Dr. F. F. Lucas, is a member of the technical staff of the Bell Telephone Laboratories, New York City. Manuscript received February 9, 1935.

cases, I believe that we have accomplished a very close approximation.

"Given good objectives to start with, there is probably as much to be gained in resolution, by improvements in the technique of preparing specimens for examination as by developing more powerful lens systems. As a matter of fact, the improvements in resolution attributed to superior lens systems can only be realized in practice by more careful preparation of the metal surfaces to be examined, . . .

"That we can obtain real images of details which measure but a few hundred atom diameters across will be clear from some of the photographs which follow. We shall also see clearly defined details of structure which by actual measurement are only a fraction of the wave length of the light used."

In principle the preparation of an iron or steel specimen for microscopic examination is relatively simple but in actual practice the fulfillment of all requirements seems a very difficult task. If it suffices for one's purpose to see under the microscope only the grains of an annealed steel specimen at a low magnification and with a very low order of resolution, the operation becomes relatively simple. It is only necessary to turn back the pages of metallographic history and follow the recommendations in use twenty years ago.

At that time metallographers were content to look at steel specimens with relatively low power microscopes. They recognized the constituents pearlite, sorbite, troostite, martensite and austenite. Pearlite was resolved into its lamellar form; sorbite and troostite baffled resolution and were regarded as uncoagulated transition products. Martensite was a needle-like structure in a solid solution, austenite. Very little was known about solid solutions, age hardening and precipitation phenomena. The development of the X-ray spectrograph and the high power microscope offered new approaches to the study of metal structures. It became apparent that the constituents named above were in reality gross details of structure, though by no means to be overlooked in the appraisal of the physical properties or characteristics of a steel specimen. The real answer to the hardening of steel and to variations in physical properties lay in part at least in the minute structural details of the recognized constituents of steel.

The steel maker, the physical chemist and the metallographer have evinced a lively interest in the dirt or inclusions to be found in steel. These vary in size from particles which can be seen with the

unaided eye to those which are so small as to be at the vanishing point of microscopic vision. Some of these inclusions are simple compounds—others are complex and may be composed of two or more compounds. The inclusions may be firmly seated in the metal or they may be held by a weak bond. Some are hard and some are soft. It has been shown in another publication[2] that the trend of a fatigue crack may be largely controlled by the presence of solid nonmetallic inclusions. The smallest visible ones exert their influence.

Even a metal specimen of very high purity is not uniform because it is composed of small grains differently oriented. At grain boundaries where the orientation changes there is a tendency for specimens to react differently to polishing and etching operations and this applies even in relatively pure metals.

In a well made tool steel bar one inch in diameter and of about one per cent carbon, the chemist would find by analysis of drillings taken at different places along the diameter of the bar a high order of uniformity in the results of carbon determinations. However if we attack the problem metallographically rather than chemically we find quite a variation in the distribution of the carbide. For example when the carbides are in the spheroidized condition, analysis by mathematical methods of the micrographs taken at 1000 diameters indicates that the carbon content in some fields may be as high as 1.65 per cent and of course correspondingly low in others. The carbide particles may vary from approximately 65,000 per square millimeter to as many as 140,000.

Calculations are based on an area on the specimen 0.004 inch in diameter. This field is neither large nor small as the metallographer considers such things. If a smaller field is used the variability is increased; if a larger field, it is decreased. But the diameter of this field compared to the actual width of a grain boundary is enormous. Yet unless we exercise care grain boundaries are eroded in the polishing operation.

It is not surprising then that a specimen of well made iron or steel presents some difficulties in polishing to a plane uniform surface. In fact, our best polishing technique is probably a crude approximation.

In the preparation of a metallurgical specimen it is desirable to have a specimen about one inch in diameter if this can be arranged.

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[2]F. F. Lucas, "Observations on the Microstructure of the Path of Fatigue Failure in a Specimen of Armco Iron", TRANSACTIONS, American Society for Steel Treating, Vol. 11, No. 4, 1927, p. 531.

A round specimen is preferable to a square or rectangular one because it is easier to manipulate in the fingers and less likely to be caught by the polishing cloth. The specimen should be about one-half inch in height. If the case or outer edge of the specimen is to be studied, it will be necessary to block the specimen to avoid rounding the edges on the lap wheel. Formerly it was customary to block or mount small or irregular shaped specimens in some fusible alloy such as Wood's metal. Some metallographers employed lead or solder for this purpose. The writer has never found such mounting methods very satisfactory. When the structure in the case or at the extreme edge is to be studied, least rounding of the edge will result when the specimen is rigidly clamped between two steel plates. Of course this method can only be applied successfully to square or rectangular specimens having straight edges. Even then the method has disadvantages because the grit used in polishing will get trapped in and about the clamping plates and holding screws. When the polishing is completed the specimen can be removed from the clamp and thoroughly cleaned before etching and nothing but the specimen itself need be placed in the etching reagent. At times this is a distinct advantage.

Perhaps the best general practice is to mold the specimen in bakelite when circumstances will permit. Bakelite mounting, in my opinion, is superior to all other methods of mounting, except when the temperature of bakelite molding is detrimental. For example if one wished to study the "as-quenched" structure of a hardened steel, the temperature necessary to mold bakelite would temper the specimen and profoundly alter the "as-quenched" condition. Otherwise everything appears to favor the bakelite method.

The ideal specimen is one about ¾ to 1 inch in diameter without mounting media of any kind. The height of the specimen should not be more than ½ inch, otherwise difficulty will be encountered in maintaining a flat surface. For smaller specimens the height should be proportionately less. Specimens ½ inch or smaller in diameter should be mounted or blocked.

The first step in the preparation of the surface is to grind one face of the specimen flat. For this purpose we use a bench grinder which has been modified so that a stream of cold water may be directed against one side of the wheel. The wheel is Aloxite Brand - 60 Grit - Grade J - Bond 31 measuring 6 by 1 inch and revolves at 3450 revolutions per minute in a vertical plane. The specimen is

Fig. 1—Photograph Showing Aloxite Paper on Bench Plate and Method of Rough Polishing Specimens.

held with the fingers against the flat surface of the wheel, and a stream of cold water is directed on the wheel just above the position of contact with the specimen. When it is desired to study "as-quenched" structures the grinding operation should be carried out if possible before heat treatment. Grinding wheels should not be used if their surface is clogged or scored. The edges of the specimen should be beveled about $\frac{1}{32}$ inch on the grinding wheel. If this is not done the paper work to follow will produce a sharp, knife-like edge on the specimen which is liable to catch and tear the lap.

The early work on the specimen is of great importance and should in no way be neglected or hurried; otherwise the imperfections of grinding and of the following paper work will not be removed by the final polishing operations. As a result the surface of the specimen will be in a worked condition and will develop roughness, scratches or cross marks like the rulings of a scale when the specimen is finally etched. All of these conditions are artifacts and have no particular significance as far as the structure is concerned, except to indicate that the early work was improperly done.

The grinding and paper work on the specimen is a matter of producing a finely cut surface in one direction and then removing it completely by a finer cut surface established in a direction at right angles. In turn each surface is removed by finer cuts or scratches until the surface of the specimen approximates a rough polish. The present author does not recommend circular lapping except for the final polishing operations.

From the Aloxite wheel the specimen goes to No. 240 Aloxite paper on a bench plate. See Fig. 1. The paper is supplied in sheets measuring 9 x 11 inches and generally is used dry.

Oils, liquid soaps, glycerine, glycerine and water mixtures, etc., may be used on the papers if desired. For iron and steel, experience teaches that best results usually are secured with dry paper except when it is necessary to avoid surface tempering. Hardened tool steel specimens containing white martensite will start to precipitate carbides unless the specimen is kept cool during the grinding and paper work. The martensitic needles in a slightly tempered specimen appear mottled or light brown instead of white.[3, 4] A change in color from white to brown indicates tempering. When it is desired to study the "as-quenched" condition of specimens, the grinding should be done before heat treatment, the heat treatment must not decarburize the surface of the specimen and all paper work should preferably be done under water or with the water-glycerine mixture. Unless precautions of this sort are observed the subsequent metallographic investigation will disclose the structure of a tempered specimen and not the true "as-quenched" structure.

The specimen is held firmly in the fingers and pushed back and forth slowly under light pressure the entire length of the paper.

[3]F. F. Lucas, "Further Observations on the Microstructure of Martensite", TRANSACTIONS, American Society for Steel Treating, Vol. 15, No. 2, 1929, p. 339.

[4]F. F. Lucas, "A Resumé of the Development and Application of High Power Metallography and the Ultra Violet Microscope", *Proceedings Amsterdam Congress*, International Association for Testing Materials, September, 1927.

The direction of grinding should be across the previous wheel scratches and this grinding operation should be continued until the wheel scratches are completely removed and no traces of them can be seen with a 6 power hand magnifier.

The Aloxite papers are quick cutting and appear to be very uniform. Unlike certain emery and other papers they do not clog or glaze. They have been chosen for this work because of their uniformity and free cutting properties. When a sheet of paper has been used until the grit is dulled it should be discarded and a new sheet substituted.

Of course the papers must be handled and stored with care so that they do not become contaminated with coarse grit or dirt. It has been found that storing a few sheets of each grade of paper in a separate heavy paper envelope is a very convenient and clean method. Formerly a drawer with separate vertical compartments for each paper was used but this method did not prove satisfactory and was superseded by the envelope idea. The envelopes are stored in a drawer having a horizontal compartment for each grade of paper.

From the No. 240 paper the specimen is ground in turn on the No. 280, No. 320 and No. 400 Aloxite papers. On each paper a new set of uniform scratches is established across the preceding scratches until the latter are completely replaced by a finer set. After completing the work on each paper, the specimen, the hands and the bench plate are wiped clean to remove all traces of the grit.

Too much emphasis cannot be placed on the grinding and paper work. It is here that a good foundation is laid for the final polishing operations and if a specimen is found which requires an unusually long time to polish or which develops a rough surface with here and there a few deep scratches that persist one may be quite sure that the difficulty lies farther back in some step of the paper work which was not properly carried out.

In the average steel specimen the grinding and paper work should be completed in about ten or fifteen minutes.

After finishing on the No. 400 paper the specimen and the hands should be thoroughly washed as the specimen is now ready for the preliminary polishing operation.

The polishing operations are carried out on horizontal laps. (Fig. 2). These laps consist of metal disks about 6 to 8 inches in diameter covered with fine woolen broadcloth for the preliminary lap and with the finest "kitten's ear" broadcloth for the final lap. The

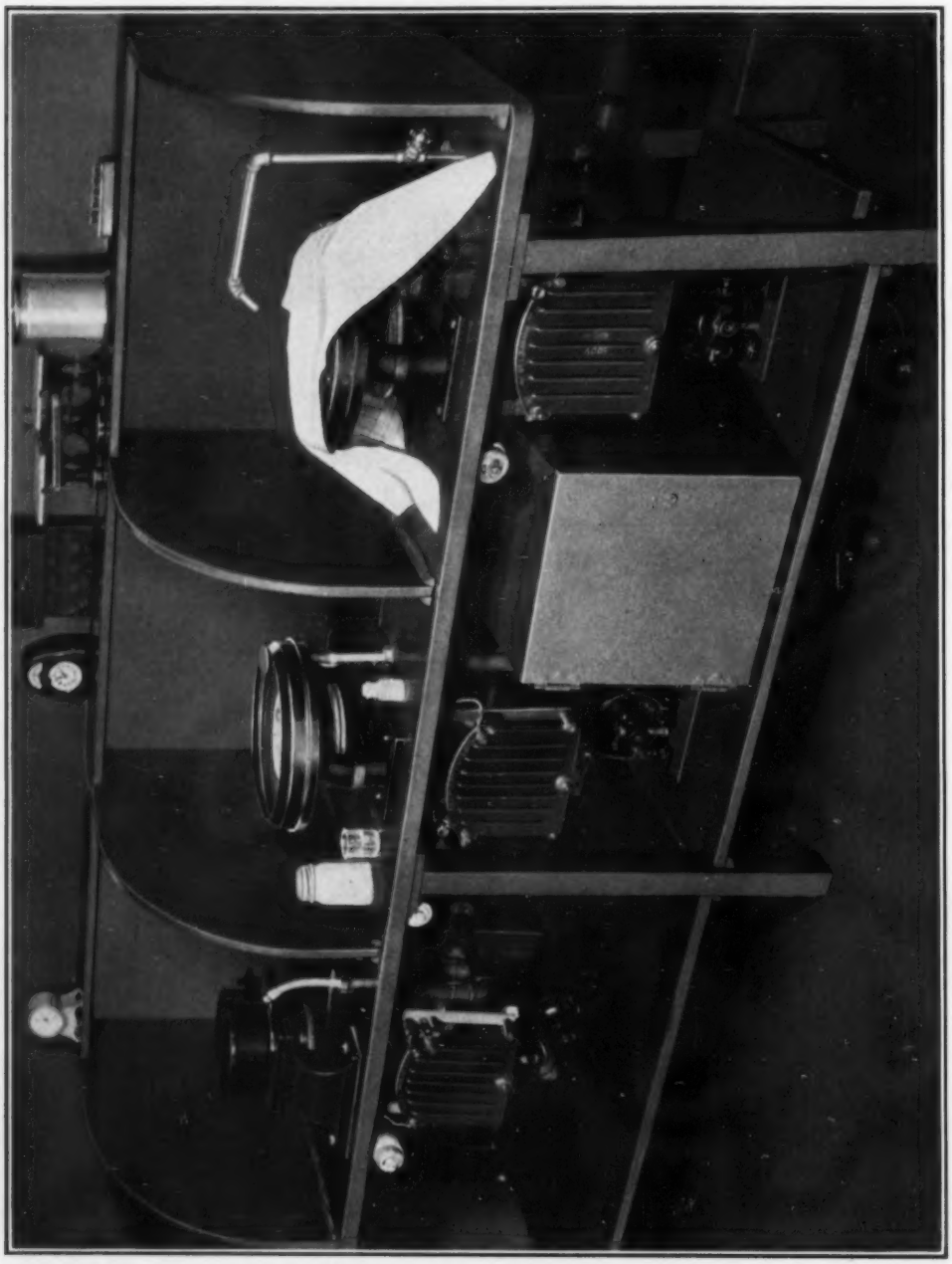


Fig. 2—Photograph of Bench and Horizontal Laps for Polishing Specimens.

laps should run true in a horizontal plane. I find it convenient to use a metal ring or hoop about the rim of the lap wheel for the purpose of holding the cloth securely in place. A soft brass strip measuring about $\frac{1}{16}$ by $\frac{3}{8}$ inch in cross section is formed into a hoop by soldering and made to fit very tightly over the lap wheel and the broadcloth covering. The broadcloth covering should be well soaked in water before

it is applied to the wheel and should be large enough so that one can grasp the edges and pull the cloth very tightly across the wheel face. A loose lap cloth will catch the specimen and oftentimes the specimen will be violently snatched from the fingers and its surface damaged by contact with the guard rim of the lap wheel. Moreover a loosely stretched lap cloth is more apt to pit and erode the specimen.

Any good horizontal lap wheel can be used as described. However, one of poor mechanical construction, with unprotected bearings and with some form of friction plate drive is to be avoided. It is desirable to have the speed of the driving motor controlled by a rheostat.

For the preliminary polishing operation a speed of about 500 to 600 revolutions per minute is employed. A separate polishing head or machine is used for the final polishing operation. It would be decidedly poor practice to carry out both preliminary and final polishing operations on the same lap because of the probability of contaminating the fine abrasive of the final polishing operation by the coarser abrasive from the preliminary polishing.

Having stretched the wet broadcloth lap tightly on the polishing head a level teaspoonful of No. 600 alundum powder is rubbed out with water to a thin paste so that it covers a circular area about 5 inches in diameter at the center of the lap. Another teaspoonful or two of the same powder is placed in a clean, 2-ounce, wide mouth, salt bottle. The bottle is nearly filled with water and stoppered with a cork which has a "V" notch cut in its wall. Covering the opening of the notch with the thumb the bottle is shaken to disperse the powder. As the polishing proceeds with the specimen held in the right hand, the lap is kept charged and moistened by shaking a few drops from the bottle at regular and frequent intervals. The small bottle held in the left hand makes a very convenient arrangement and is superior in the writer's opinion to the automatic forms of droppers with stirring devices, drip pipes, shut-off cocks, etc. The use of these devices has been given up. The objection to the automatic droppers is that they allow the grit to settle and it is more work to clean them after use than it is to resort to a simple little bottle arrangement which can be used to direct the grit where it is wanted and when the job is over the bottle can be cleaned by flushing under a tap of water.

The first operation in the preliminary polishing is to remove all

Fig. 2—Photograph of Bench and Horizontal Laps for Polishing Specimens.

traces of the No. 400 Aloxite paper scratches. The specimen is moved back and forth from center to periphery of the lap under a moderately light pressure. The specimen is oriented so that the lap scratches cut the paper scratches at about right angles. Since overpolishing, dry polishing or polishing in relief is to be avoided, the specimen must be kept under close observation. To do this it is merely necessary to rinse it off under a tap of water and inspect the surface with a 6-power hand magnifier. After 5 to 10 minutes of polishing the paper scratches should be removed. If a much longer time is required to remove the paper scratches, it may be inferred that the paper work has not been properly carried out. All steel specimens do not react the same to the polishing lap so that no really fixed rule is possible. For example, a hard steel will usually polish much faster than a tough austenitic steel. The only safe criterion is to examine the surface of the specimen at frequent intervals. If certain of the scratches persist while most of the others are quickly removed those which persist were produced originally by a coarser grit than the others. Time will be saved and a more satisfactory surface produced if the specimen is returned to a fresh and clean sheet of No. 400 paper and a new paper surface established at right angles to the direction of the persistent scratches. Before returning the specimen to the alundum lap the lap cloth should be thoroughly washed out with clean cold water and soap. The polishing head itself should also be well cleaned before the lap cloth is replaced.

There are no short cuts which will mitigate lack of cleanliness in the polishing operations or by which faulty workmanship at one stage of the process may be corrected at another. If one discovers something wrong or if too much time is being consumed in a given operation it is an excellent rule to go back one operation and start over. The entire time required to produce a critical surface on a hardened steel specimen should be forty to sixty minutes so that polishing a specimen is not necessarily such a tedious task. It becomes tedious however when one loses sight of the fundamental principles or tolerates faulty workmanship. It may be interesting to know that students with little or no knowledge of the subject have mastered the art quickly under personal instruction along the lines suggested above.

The specimen has now reached the finishing stage on the alundum lap. To the eye it should present a uniform surface and if a rather hard steel the surface will act as a mirror yielding a fairly good

image. As the surface is examined in strong reflected light by the aid of the 6-power magnifier many very fine scratches due to the alundum grit will be seen and the inclusions will appear considerably enlarged. If the section happens to be a transverse one the inclusions will be strung out in the form of crescents or "comets." This is due to the fact that thus far the lap has traveled by the inclusions from one direction only. The leading side of the inclusion will be a sharp line and a "comet tail" formation of the metal surface will extend from the opposite side. Overpolishing accentuates this condition, erodes the softer inclusions and produces artifacts which have no bearing on the real quality or structure of the steel. Pitting may easily result and grain boundaries may also be eroded. If the specimen contains both martensite and troostite careful workmanship is necessary, otherwise the troostite will erode much faster than the martensite. Other constituents of varying hardness and resistance to abrasion will react in much the same way.

The next operation is to improve the mirror qualities of the surface and define the inclusions sharply. This is done by rotating the specimen so that in one revolution of the specimen about the lap the latter will have approached any given detail from all possible angles. Assuming the lap is turning counter clockwise the operator revolves the specimen slowly about the lap in a clockwise direction. At the same time he may slowly rotate the specimen in his fingers. The specimen should be examined at frequent intervals; for this purpose the surface should be rinsed under a tap of water and dried with bibulous paper. The surfaces should be examined with a metallurgical microscope using a plane glass vertical illuminator. A magnification of about 100 diameters will suffice. As the polishing is continued the inclusions become sharp and well defined and the "crescents" or "comet's tails" disappear. At this stage the specimen is finished so far as the alundum lap is concerned. The surface will be traversed by very fine scratches from the No. 600 alundum grit but the scratches should be very fine and all of about the same magnitude. The time required for this semi-final polishing by rotating the specimen on the alundum lap should be about 4 to 6 minutes. The specimen should then be thoroughly washed and dried. Bibulous paper as a blotting medium or a clean linen laboratory towel may be used for drying.

The final operation of polishing requires some preparation both as to the cloth for the lap and the abrasive to be used on the lap.

The late Dr. Rosenhain was the first, we believe, to recommend magnesium oxide as a final abrasive but this abrasive was under experimentation very soon after in the United States. This was nearly fifteen years ago and despite all efforts to develop a more stable and satisfactory abrasive, magnesium oxide still stands in a class by itself. Much work has been done in this laboratory in the past ten years in an attempt to improve on the commercial magnesium oxide. Magnesium oxide has one bad chemical characteristic of converting to the carbonate with a change in particle size by agglomeration. Very large gritty particles appear if the powder is exposed to the air and to humidity. The oxide may be used on a cloth lap all day providing it is kept covered with water, but if allowed to dry out the lap is utterly useless until it has been thoroughly washed in rather strongly acidulated water and all trace of the powder removed.

To offset the drying out of the lap the writer has employed a mixture of one-half water and one-half glycerine instead of water to moisten the lap. This mixture keeps the lap thoroughly wet, prevents formation of the gritty particles and does not seriously impair the cutting properties of the abrasive. For some specimens, however, it will be found that the water-glycerine solution will slow down the polishing. For such specimens we use water only.

There are two grades of commercial magnesium oxide, one of which is prepared by grinding and the other is a precipitation product. Either is satisfactory as a metallographic polishing abrasive providing it is free from the hard gritty particles. Perhaps as good a test as any is to rub out a small quantity of the powder in the palm of the hand using the forefinger. Repeated tests should be made and if a single hard gritty particle is encountered the powder is useless for critical work until refined. It is next to impossible to secure a satisfactory commercial powder so a quick and convenient mode of refining magnesium oxide by air flotation has been developed.

Fig. 3 shows details of the flotation chamber used for the purpose. It is easily made in any tinsmith's shop; may be easily assembled or dismantled and can be cleaned without difficulty. About five pounds of commercial heavy magnesium oxide is placed in the cone-shaped hopper at the bottom. In the bottom of this hopper is an air nozzle having a large number of small apertures. The nozzle is connected to a compressed air line in which there is an air filter. By means of a suitable rubber gasket the hopper is connected airtight to a vertical pipe. To the upper end of the vertical pipe

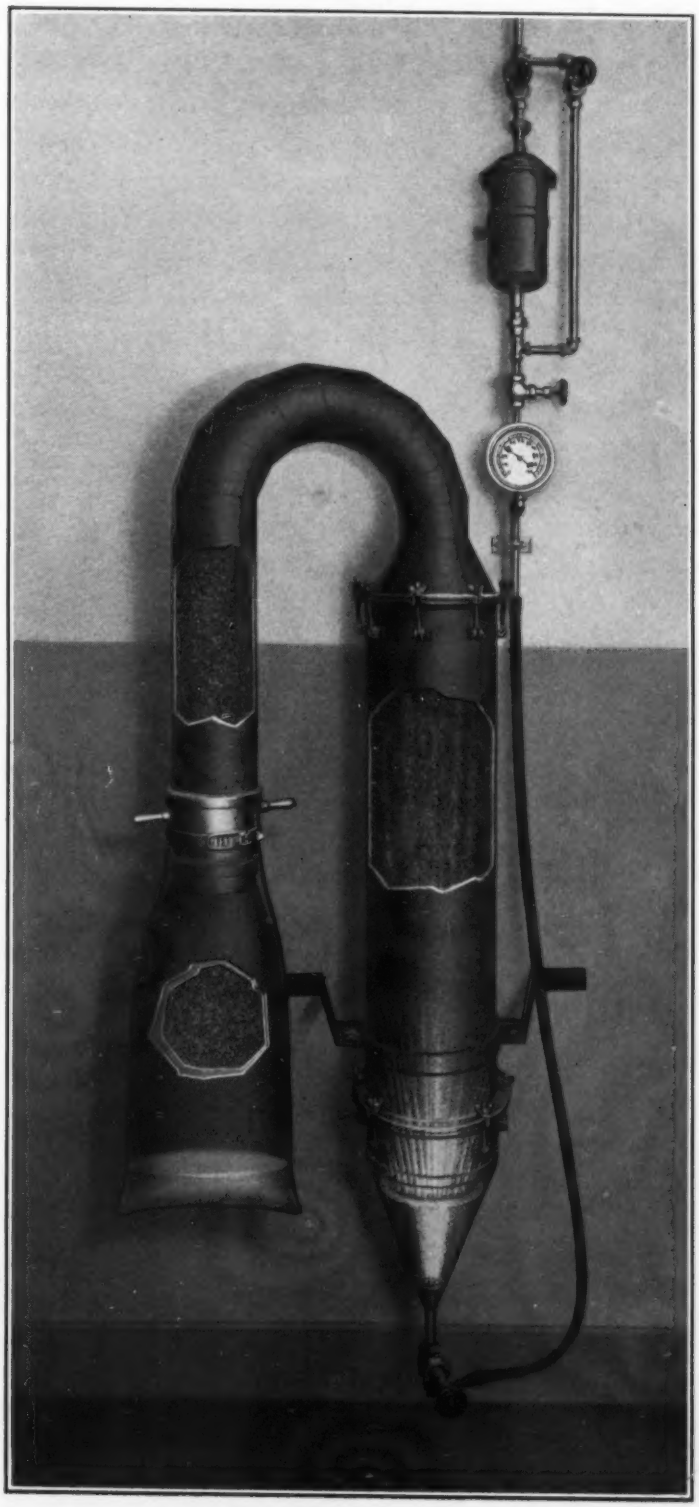


Fig. 3—Sectionalized Drawing Showing Details of Flotation Chamber Used in Preparing Grit-free Magnesium Oxide.

is similarly secured a curved pipe leading downward. Shown in Fig. 3.

The lower end of this exhaust pipe has a screw fitting to which may be attached a porous paper bag of about the dimensions of an ordinary flour sack. This paper sack is secured to the collar of the fitting by means of a paper adhesive tape known as "Scotch tape", readily procurable in any store handling draughtsman's supplies. Ordinary surgical adhesive tape or the common electrical friction tape might be used as a substitute. What is desired is a strong air-tight seal. Over the paper bag is secured by a convenient lever fastener, a porous cloth bag of the general type used on vacuum cleaners. This bag is merely used as a safeguard in case the air pressure should cause the paper bag to burst. Now and then a defect or weakness occurs in paper bags and unless some provision is made, such as the cloth bag, the fine powder will be blown far and wide. One clean-up job suffices to demonstrate the forethought and expediency of the cloth bag idea. As here described the apparatus may be used safely in any laboratory.

By varying the height of the vertical pipe some control can be exercised over the fineness of the resulting powder. Two lengths are employed. One is 35 inches and the other 78 inches. Both are 9 inches in diameter. They are readily interchangeable. If the former is used, a coarser, quicker cutting powder results which will be found satisfactory for most work providing too high an air pressure is not applied for blowing. The longer pipe produces a finer powder and a lessened yield but for finishing work on critical specimens this abrasive leaves little to be desired.

When ready for use the air is gradually turned on until the bag is fully distended and under considerable pressure. We employ an air line pressure of about 30 pounds per square inch. The powder is blown upward and the finer particles are carried over the "goose-neck" into the paper bag where they are collected. The coarser and heavier particles drop back. The operation is a continuous one requiring little attention except perhaps once in a while to tap the hopper in order to prevent the powder from collecting about the walls. The yield is large and one day's operation will provide a month's supply of fine magnesium oxide.

When sufficient powder has been collected in the bag, the air is shut off and the bag removed. The powder is placed in pint fruit jars and the uncovered jars are placed in a drying oven at a temperature of about 100 degrees Cent. for about twelve hours. While

still hot the jars are sealed tightly with covers and rubber rings, and allowed to cool. In this condition the powder will seemingly keep indefinitely.

A typical particle size determination of the finished powder, by ultra-microscopic methods has yielded the following analysis:

26 per cent of the particles are 0.08 micron in diameter
42 per cent of the particles are 0.17 micron in diameter
26 per cent of the particles are 0.25 micron in diameter
6 per cent of the particles are 0.33 micron in diameter

The diameter of the average particle was 0.176 micron. This powder was secured by the use of the shorter pipe.

The particles are difficult to photograph by means of the ultra-violet microscope[5] because they transmit ultra-violet light and therefore are invisible in the usual mounting media. Some research seems necessary to find a suitable medium. The ultra-violet method of particle size analysis is a very accurate method whenever it can be applied. The ultra microscopic method is an approximation but experience has shown that the particles in the range indicated above appear somewhat larger than they actually are, say, by the ultra-violet method of analysis. Since a given small particle appears larger when photographed with red light than with blue light and likewise larger with blue light than with ultra-violet light, the whole scheme of particle size measurement should be made relative to some base wave length. With an intense source of light the ultra microscopic method is really the most effective because the smaller particles are made to appear a little larger and one can detect smaller particles by ultra microscopic methods than by any other method. For grading purposes such as the present example the ultra microscopic method is a reliable one providing one makes due allowances for the peculiarities of the system as mentioned above.

The polishing cloth of kitten's ear is prepared by soaking it over night in acidulated water. A 2 to 4 per cent solution of hydrochloric acid will be found satisfactory. This soaking operation softens the cloth and it is best always to prepare a new cloth by this treatment. After the soaking operation the cloth is well washed in cold running water to remove all traces of the acid. The excess water is squeezed out by hand and the cloth stretched tightly on the polishing lap.

A small quantity of the processed magnesium oxide powder,

[5]F. F. Lucas, "Late Developments in Microscopy," *Journal*, Franklin Institute, Vol. 217, No. 6, June 1934, p. 661.

Fig. 4—Photograph Showing the Manner in Which the Specimen is Polished on the Magnesium Oxide Lap by the Rotation Method.

perhaps equivalent to two level teaspoons, is placed in the center of the lap and mixed with water by means of the fingers to the consistency of a thin cream, and spread out over the central area of the lap. About the same quantity of the powder is shaken up with water or with water and glycerine in a suitable shaking bottle as previously described for the alundum powder. This is used to provide fresh abrasive and to keep the lap wet while polishing.

The thoroughly cleaned specimen is now polished on the magnesium lap by the rotation method as described for the semi-final polish on the alundum lap. (Fig. 4). The speed of the lap is 400 to 500 revolutions per minute. It is a good plan to use an interval timer and to set it to ring after fifteen minutes. If the work

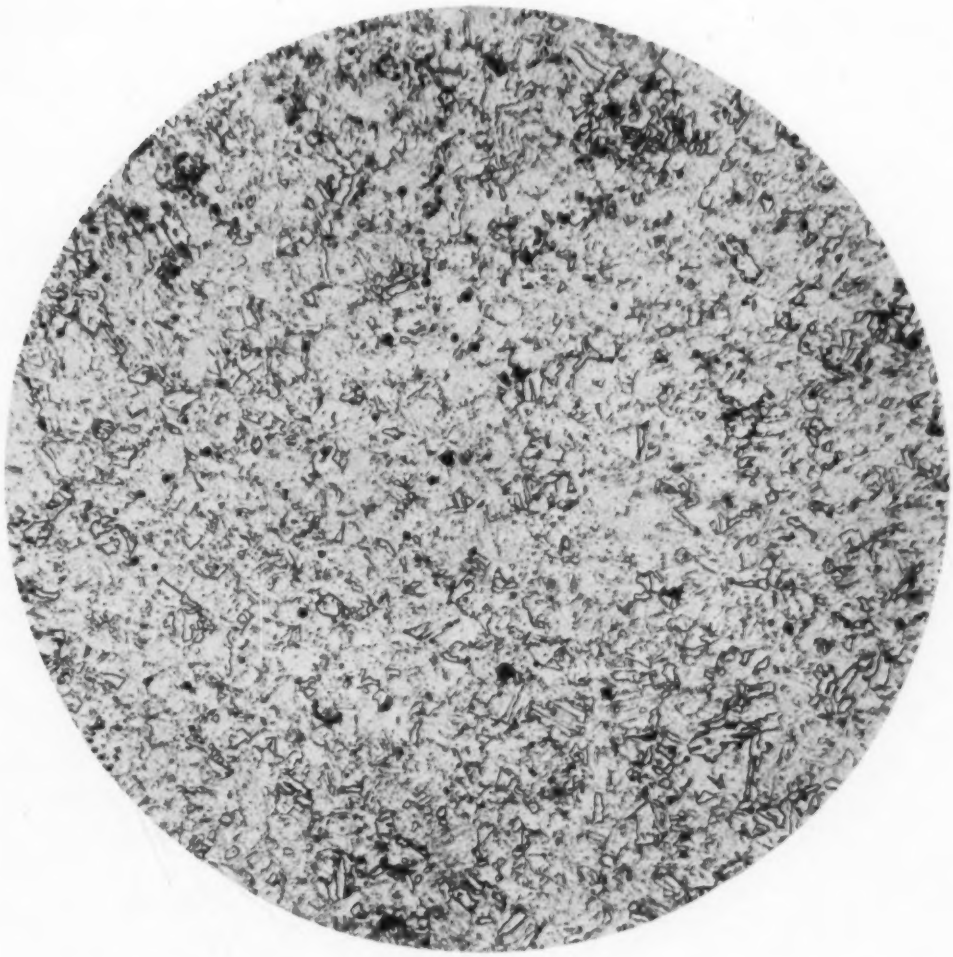


Fig. 5—Stainless Iron Quenched in Oil from 1750 Degrees Fahr. (955 Degrees Cent.) and Tempered 1 Hour at 1300 Degrees Fahr. (705 Degrees Cent.) × 200.

has been properly conducted the specimen of iron or steel will, at the end of the interval, have developed a beautifully polished surface, brilliant and mirror-like, with inclusions standing out sharply defined and no pitting of consequence. Practice and experience throughout the past ten years have set the interval of fifteen minutes as a good guide, and as a rule one need not examine specimens until they have been polished from 12 to 15 minutes. If the surface is not perfectly smooth and brilliant, polishing should be continued a few minutes longer. On occasions we wash out the lap cloth and finish with the very fine magnesium oxide powder.

When the polishing operation is about finished the lap is moistened with liquid soap and polishing is continued for about a

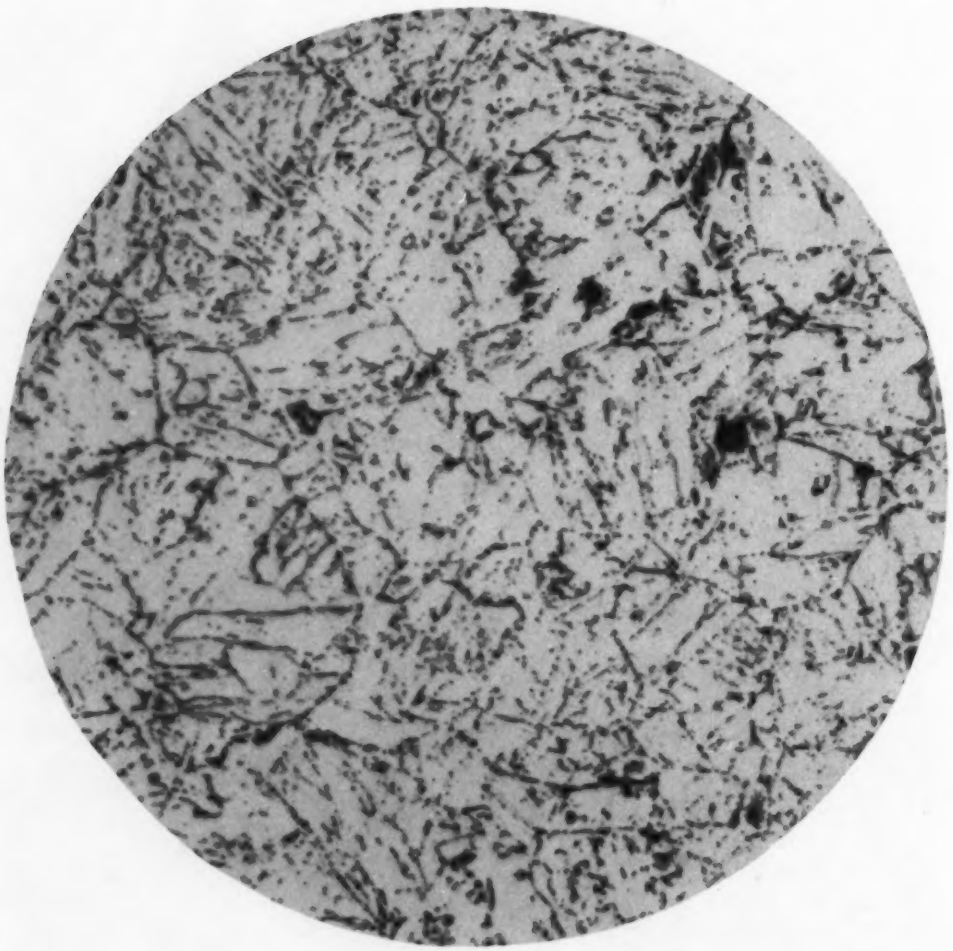


Fig. 6—Stainless Iron Quenched in Oil from 1750 Degrees Fahr. (955 Degrees Cent.) and Tempered 1 Hour at 1300 Degrees Fahr. (705 Degrees Cent.) × 1000.

minute. The soap makes it easier to wash the surface of the specimen and rid it of the magnesium oxide powder.

The washing is done under a tap of warm water and the surface of the specimen is lightly brushed with absorbent cotton of the best grade. The cotton is wet with liquid soap. The running water should be as hot as the hand can stand — as the specimen will dry quicker when heated up to this temperature.

If the surface is not cleaned carefully the adhering particles of magnesium oxide will dull the mirror surface of the specimen, and too, they may be mistaken for inclusions. Unless the specimen is thoroughly dried immediately the surface may tarnish, especially around some of the inclusions. Drying is accomplished

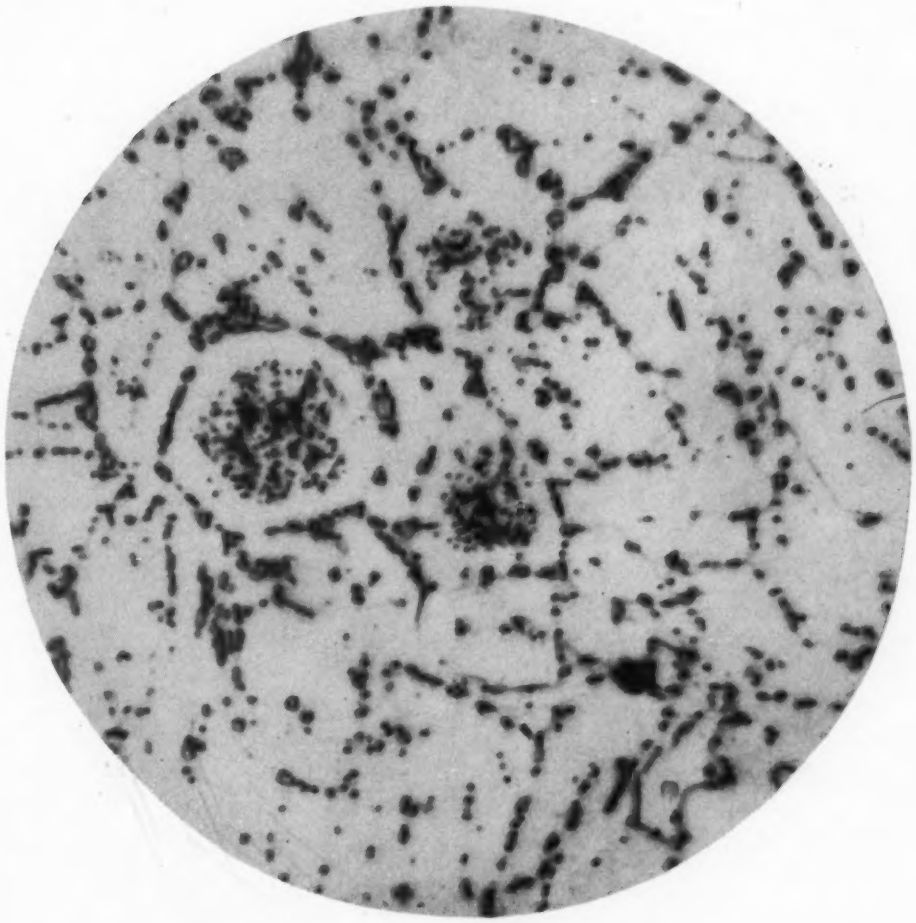


Fig. 7—Stainless Iron Quenched in Oil from 1750 Degrees Fahr. (955 Degrees Cent.) and Tempered 1 Hour at 1300 Degrees Fahr. (705 Degrees Cent.) × 4000.

effectively by taking the specimen from the hot water, shaking it, placing it face downward on bibulous paper and then quickly immersing it in ethyl alcohol. It may then be removed from the alcohol and dried in a stream of warm air. For this purpose an ordinary hair dryer is best. The specimen should be placed immediately in a desiccator and kept there whenever it is not in use and whether unetched or etched.

After polishing a specimen, the lap should be covered with the water and glycerine solution or with plain water; a clean cloth is placed above the lap to keep out dust or dirt. By these precautions the lap will be kept in good condition for the day. When through using the lap for the day the kitten's ear cloth should be thoroughly

washed out with soap and water after which it should be stored for future use in a covered glass receptacle containing water acidulated with hydrochloric acid.

For the purpose of etching the specimen four 100-cubic centimeter glass beakers are arranged side by side under a strong light. About 50 cubic centimeters of absolute ethyl alcohol is placed in the first beaker and about the same quantity of 95 per cent ethyl alcohol in the other beakers. The usual alcoholic reagents such as 10 per cent nitric acid, 5 per cent picric acid, 10 per cent hydrochloric acid, etc., are prepared and kept in glass-stoppered bottles. Assuming it is desired to etch a hardened steel specimen with nitric acid about 2 to 4 cubic centimeters of the prepared etching reagent is added to the first beaker containing the absolute alcohol. In the event the specimen is one of the modern alloy steels of corrosion resistant properties, the recommended etching reagents are used full strength. The mixture is stirred with a clean dry glass rod to promote uniformity of solution. Using platinum-tipped or other suitable noncorrosive forceps the specimen is carefully lowered into the etching solution and the beaker agitated. A stop watch is used for timing the etching period. The surface of the specimen is closely observed under a strong light. As the surface etches very slowly its mirror-like properties will be dulled. By watching the surface of the specimen and noting, for example, how the image of a lamp bulb conveniently placed for reflection dims one can exercise excellent control over the etching. Experience soon teaches when the etching should be arrested. The time of etching is noted on the stop watch and the specimen quickly washed in succession through the three alcohol washes. From the last wash it is placed in a stream of warm air, and quickly dried.

The specimen should now be examined under the microscope and if insufficiently etched the process is repeated. The elapsed time of the first etching period as recorded by the stop watch allows one to judge with reasonable accuracy the duration of the second etching period. By etching the specimen gradually control of contrast can be secured. Brilliancy of the photographic image will depend to a considerable extent on the delicacy with which contrast has been developed in the etching operation. An under-etched specimen lacks contrast and an over-etched specimen is one which has had its fine detail obscured and often obliterated. When a specimen is over-etched it should be returned to the No. 400

Aloxite paper and repolished from that stage. If returned only to the final lap for repolishing the detail in relief will be rounded and the results are not regarded as satisfactory where the ultimate in resolving power is desired.

DISCUSSION

Written Discussion: By V. O. Homerberg, associate professor of physical metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

The present paper by Dr. Lucas represents another valuable contribution to this important subject. I concur with the viewpoint that the proper preparation of a sample is highly important for correct interpretation of the structures by microscopic examination after suitable etching.

Within recent years metallographers have come to realize that higher resolution in their microscopic investigations may be limited fully as much by the preparation of the metallic surfaces as by the lens system employed. As an example, the true structure of troostite formed on quenching has been determined as a result of the combination of these two factors.

The mounting of specimens in bakelite prior to polishing excels all other methods provided that the specimen is unaffected by temperatures up to 200 degrees Cent. (390 degrees Fahr.).

Although magnesium oxide is highly desirable for final polishing, it is difficult to use for class work, such as at Massachusetts Institute of Technology, where many students use the polishing equipment, since it is practically impossible to keep it free from carbonate. For ordinary work, therefore, alumina is used for the final step in the polishing operation. After dry polishing a suspension of No. 600 carborundum is used on 12-ounce duck; a 20-minute suspension of levigated alumina on broadcloth is used for the second operation; and finally a 60-minute suspension of levigated alumina plus soap solution on velveteen is used for the third operation. For fine work, such as in the study of nonmetallic inclusions, a 2-hour suspension of alumina is recommended.

The method of polishing for a set time of 12 to 15 minutes on the last lap is desirable since it will prevent any attempt to hurry the final operations and will therefore tend to form the habit of careful polishing.

A discussion of the flotation chamber for preparing grit-free magnesium oxide is welcome since much of the pure magnesia on the market contains considerable gritty material.

Written Discussion: By H. P. Munger, American Rolling Mill Co., Middletown, Ohio.

There is no question but that the art of polishing metallographic specimens has been developed to a high degree in the author's laboratory. The present paper will be very useful to men who are engaged in metallurgical research.

In the mounting of samples to be polished it has been pointed out that certain heat treated samples cannot be mounted in bakelite because of the effect of the temperature attained during the molding of the bakelite. Since slightly elevated temperatures may change the structures profoundly, it is sometimes desirable to mount samples in a medium at room temperature. We have had very satisfactory results mounting irregularly shaped samples in a

mixture of litharge and glycerine. The surface of the sample to be polished is placed on a flat plate. A metal ring, usually brass, is placed around the specimen and a thick paste of litharge and glycerine is poured into the ring. The paste will set up in a few hours and the specimen may be polished in the usual manner. This method of mounting specimens has proved very useful when a metallographic examination must be made of small irregularly shaped samples.

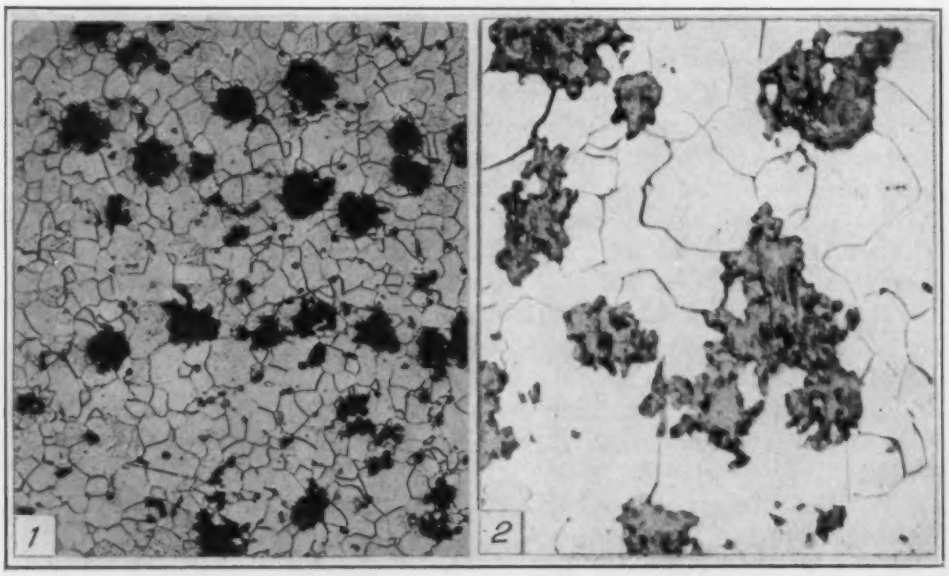
Written Discussion: By Louis Ziffrin, metallurgist, Deere and Co., Moline, Illinois.

It is somewhat disappointing in reading this paper by Dr. Lucas in that there are no photomicrographs presented on gray cast iron or malleable cast iron.

I believe that the metallographer today would indeed feel elated to know that his work was to be confined to steels, whether they be plain carbon steels, high speed steels, or stainless steels. We must admit any one of which it is by far much easier to prepare than is gray cast iron or malleable cast iron.

When we consider that in the case of a hardened steel, we are dealing with a material that is almost at a maximum in hardness we know that very little difficulty will be had in retaining any inclusions that may be present.

In the case of cast iron, we are dealing with a considerably softer material; malleable cast iron, which is very soft, and gray cast iron, which is also



relatively soft. In both cases, it becomes extremely difficult to retain the graphite or inclusions, due to the ease with which the metal surrounding the graphite or inclusions can be polished away.

I have shown two photomicrographs, Fig. 1 prepared by the present writer several years ago showing the temper carbon completely wiped out, this microphotograph being taken at 100 ×; Fig. 2 showing the temper carbon undisturbed and completely intact. This photomicrograph, at 200 ×, was taken by the writer just recently.

It is these soft materials that I feel most of us are concerned with, the retaining of this soft and friable graphite.

I have a high regard, along with the majority of metallographers, for the outstanding work of Dr. Lucas, but at this time, I must again express my disappointment in not seeing photomicrographs of the softer materials such as gray cast iron and malleable cast iron.

The proper polishing technique for cast iron micro-specimens should be just as important to the metallurgist in the steel foundry or in the manufacturing plant, because one never knows when he may be called upon to investigate such materials as cast iron or malleable cast iron.

Oral Discussion

PROFESSOR H. M. BOYLSTON:[1] On my own behalf, I wish to second practically everything that Dr. Lucas and Dr. Homerberg said, but I do want to make one or two remarks. First, for the ordinary run of mine polishing which will have to be depended upon in most commercial laboratories, I find a 4-step process sufficient and excellent. I use a solid alundum wheel, of grade 80P with plenty of water. In the second operation I use grade FF best turkish flour emery in powdered form. (Grade FF on 12-ounce duck.) In the third operation, alundum powder No. 600 on black woolen broadcloth of the order of $4.00 a yard material.

In the final operation I use a very short nap velveteen which goes under the name of Vel-Chamee, and I understand that there is a similar cloth, Selvyt. These four operations will make a very fine preparation for the specimen after a little practice, and a man can get so that he can polish an ordinary specimen in from twenty to twenty-five minutes, perhaps even a shorter time.

I have tried kitten's ear broadcloth in grades costing around $15.00 a yard, and I must say that I do not like it any better than the ordinary $4.00 woolen broadcloth, but I do like this Vel-Chamee better than either. Also I prefer Fisher's No. 3 Grade levigated alumina for the final polishing. I put it on the wheel much as Dr. Lucas does, except that I happen to use a little piece of glass tubing in the cork of the bottle. It is much more satisfactory, I find, than magnesia.

R. L. KENYON:[2] I would like to ask the author a question in regard to certain of the polishing operations. A number of years ago, Mr. Guthrie presented a paper before this Society, describing polishing methods in which to my knowledge, he described for the first time the use of a paraffin wheel to follow immediately after the dry grinding operation. Our laboratory was having considerable difficulty with pitting of specimens just at the time the paper appeared, and we received it with a great deal of satisfaction as a solution to our problems, and have used it ever since. This method consists of polishing on a molded paraffin block on top of one of the regular horizontal laps, using a soap solution in which ordinary levigated alumina is in suspension. We use no high priced specially prepared alumina, but just the ordinary run of levigated alumina for metallographic polishing which can be

[1]Professor of Metallurgy, Case School of Applied Science, Cleveland.
[2]Research Metallurgist, American Rolling Mill Co., Middletown, Ohio.

bought in 10-pound cans. This makes a very fast cutting wheel which removes all of the drying grinding scratches, and seems to prepare a very flat surface ready for the last polishing operation on cloth. We follow that paraffin wheel with a billiard cloth wheel upon which we use jewelers stick rouge. It is very easy to handle compared with the old method of applying rouge with a wash bottle.

I would like to ask the author if he has found any disadvantage to the use of such a wheel in a preparation of samples for very high power work. We find it very satisfactory for work up to 1000 diameters. I would like to know if he has any comments on its use for the higher powered work that they have described.

J. F. CUNNINGHAM:[3] Coming from Western Canada, and being concerned with metals after they have failed, in testing and in fractures, I must compliment the author, Dr. Lucas, for further information on procedure which we require very often to obtain and prove points in which claims have to be adjusted.

In reading various publications and those of the Society I have yet to see a description of preparing very small specimens such as those which I had recently worked with. A small piece of steel taken from the eyeball of a chap who had lost his eye. The mounting of this was the most difficult job yet encountered by the speaker. In using Bakelite mounting the specimen seemed to be loosened each time during the etching process. Mr. Kenyon's remarks in the discussion of this paper, regarding the use of litharge and glycerine might possibly solve a problem such as this. Papers of this class surely are of great importance to all of us, as it is interesting to know how problems are overcome in the larger laboratories and to know that good results can be obtained without the use of elaborate equipment.

H. A. ANDERSON:[4] Although I presented the paper I would prefer to have Dr. Lucas reply to these discussions, but perhaps, a few words of explanation are appropriate.

In respect to Mr. Ziffrin's request for information on polishing other types of specimens, I might call attention to the fact that this paper covers "The Preparation of Iron and Steel Specimens." Let us hope that Dr. Lucas will follow it with another paper on "Methods of Preparation for Nonferrous Alloys," involving softer specimens. I presume you are aware of the description that he gave some time ago of "The Preparation of Lead Specimens by the Microtome." This method is quite extensively used at this time for lead and other soft metals.

Professor Boylston's quicker methods for preparing metallographic specimens are of course more appropriate for the average laboratory than the somewhat elaborate methods that Dr. Lucas has described. However, all of Lucas' operations are included for adequate reasons and are justified if one is anxious to obtain the highest type of work. His continual battle is to get maximum resolution of the smallest detail within the material.

With reference to the inquiries of Mr. Kenyon, about the use of a paraffin disk, I know that Dr. Lucas has tried that, but I am of the impression that

[3]Superintendent of Testing Laboratories, Civil Engineering Dept., University of Manitoba, Winnipeg, Canada.

[4]Metallurgist, Western Electric Co., Hawthorne Station, Chicago.

he has found that abrasive particles tend to become imbedded in the paraffin. His practice is to throw away his laps and papers, or give them a thorough cleaning, and if any large size abrasive particles get into paraffin laps, this necessitates scrapping them. I want to correct what appears to be a misimpression on Mr. Kenyon's part, namely, that the Aloxite powder which is used, requires preparation in this classifier. On the contrary, the classifier is used only for the magnesium oxide which is utilized in the final polishing.

Reply by Dr. Lucas

I am much indebted to Mr. Anderson for his kindness in presenting this paper for me and am appreciative of the discussion which it evoked.

Mr. Kenyon has asked a direct question about the advantages of a paraffin wheel. Most metallographers have thought that a flat smooth lap would undoubtedly be a great improvement over the cloth covered laps. I have experimented with a number of composition laps such as waxes, soaps, soft metal, impregnated papers and cloths, etc., but have never found them of any use whatever. It is conceivable that in conjunction with an automatic polishing machine some of these smooth laps might work quite satisfactorily for certain types of work. I think it would depend on the way in which the specimen is clamped, revolved and spaced with reference to the rotating lap. Regarding Mr. Kenyon's comments and question on the use of rouge, I gave up the use of rouge either in powder or stick form about fifteen years ago and since then have never found a more satisfactory final abrasive than magnesium oxide when properly prepared. The ordinary run of magnesium oxide powder is no better than rouge, if as good.

Mr. Cunningham brings up the old question of mounting very small specimens and mentions the fact that a tiny piece of steel taken from the eyeball of an injured man failed to stay mounted in bakelite. This difficulty sometimes occurs, but usually some method of "keying" can be employed. The litharge and glycerine or litharge and shellac mount has never proved satisfactory to me, principally because small particles of the mounting medium become detached and contaminate the abrasive of the laps. I think Mr. Cunningham would find the Canada balsam method of mounting more satisfactory than litharge and glycerine, for the type of specimens he describes. This method will be found described in Professor Sauveur's "The Metallography and Heat Treatment of Iron and Steel," third edition, pages 525 to 528.

Mr. Munger also mentions the use of litharge and glycerine as a mounting medium for irregular shaped specimens.

Mr. Ziffrin expresses regret that I did not include an illustration or two of cast iron or malleable cast iron. Unfortunately I did not anticipate such a request. Last June, a number of such micrographs were exhibited by request at the A.S.T.M. meeting in Detroit. These micrographs at 1000 and 4000 diameters showed the influence of internal structural details on the trend of fatigue cracks. These details I called internal stress raisers. As Mr. Anderson has pointed out, the methods described are intended to apply to cast iron, malleable iron, etc.

The kind remarks of Professor Homerberg, Professor Boylston and the others commenting on the paper are gratefully acknowledged.

OXALIC ACID AS AN ELECTROLYTIC ETCHING REAGENT FOR STAINLESS STEELS

By George A. Ellinger

Abstract

A method for etching corrosion resisting alloys which has proved very useful is described in this paper. This method has a number of advantages among which are the following:—

1. It reveals both carbides and grain boundaries in most alloys of the 18-8 type, after suitable etching periods.

2. It is reasonably rapid in action and is not dangerous to use.

3. It affords a means for studying structures at higher magnifications.

4. Specimens do not stain after use but remain bright and may be examined months after preparation.

5. It affords an excellent medium for the etching of materials of different origin and treatment in the same specimen such as are found in welded joints.

Introduction

IT is well recognized at present that differences in composition which were formerly thought to be insignificant may have an important effect upon the properties of metals for certain types of service. Certain differences in composition can frequently be detected in the microstructure, and studies of this kind may be of great assistance in determining the suitability of these materials for specific purposes.

With the advent of the corrosion resisting alloys with a high chromium content, with or without nickel and other alloying elements, special polishing and etching techniques for the study of the microstructure became necessary. Polishing and etching of the alloys were at first difficult, but suitable technique has been developed

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as is now well known. Various etching reagents and methods have been applied, many of which proved useful for certain types of structures but entirely unsuitable for others. This was particularly true for welded specimens, in which the simultaneous revealing of the structure of both welded and base metal areas was almost impossible. Since the weld metal etched quite rapidly, it was seriously over-etched before any significant structure was revealed in the base metal. Inclusions which frequently are of much value in the study of weld metal were usually entirely removed. A knowledge of intergranular precipitation of carbides is desirable but none of the recommended reagents has proved to be entirely satisfactory or reliable.

Electrolytic etching in a sodium cyanide solution was found to be suitable for revealing carbides and was embodied by the Navy Department in specifications governing the purchase of corrosion resisting alloys. This reagent is of great value, although somewhat slow in action, but has the disadvantage of not revealing grain boundaries. It was believed, therefore, that a reagent which would reveal both carbides and grain boundaries would be of decided value for a complete study of carbide precipitation in these materials. Experience has shown that electrolytic etching is often superior to immersion or swabbing methods. Numerous reagents, known to have some corrosive attack on stainless steels, were investigated to determine their suitability as an etching reagent.

Preliminary work indicated that a reagent of sufficient reducing power to remove the oxide film from the surface was desirable, and a solution of oxalic acid in water was found to be the most suitable for general use.

Procedure and Results

The solution generally used contains 10 grams of oxalic acid dissolved in 100 milliliters of distilled water, which may be diluted if desired for specific purposes. The polished specimen is made the anode and a piece of platinum gauze, the cathode, the two being about 1 inch apart. Current from a 6-volt storage battery or from 4 dry cells connected in series is passed through the cell.

Carbides are revealed in the 18-8 (18 per cent chromium and 8 per cent nickel) type of corrosion resisting steels by 15 to 30 seconds' etching, and additional etching, 30 to 45 seconds, will reveal

Table I

Composition and Heat Treatment of Specimens

Specimen	Carbon Per Cent	Chromium Per Cent	Nickel Per Cent	Titanium Per Cent	Treatment and Nature of Sample
1	0.06	18.50	9.41	nil	Heated to 1100 degrees Cent. (2010 degrees Fahr.), cooled to room temperature in air, reheated and held at 650 degrees Cent. (1200 degrees Fahr.) for 10 minutes and air-cooled.
2	.044	18.50	9.82	0.18	Heated to 1150 degrees Cent. (2100 degrees Fahr.), quenched in water, reheated and held at 675 degrees Cent. (1250 degrees Fahr.) for 10 minutes and air-cooled.
3	.06	18.86	9.09	nil	Arc weld metal, reheated and held at 650 degrees Cent. (1200 degrees Fahr.) for 60 minutes and air-cooled.
4	.054	18.59	9.30	nil	Base metal upon which above weld was deposited. Heated to and held at 650 degrees Cent. (1200 degrees Fahr.) for 60 minutes and air-cooled.
5	.05	.....	....	nil	Aircraft engine exhaust-collector ring.
6	.06	.....	....	0.40	Aircraft engine exhaust-collector ring.
7	.10	18.9	nil	....	Chromium iron nut.
8	.08	17.66	9.30	nil	Arc weld metal, as deposited.
9	.08	18.00	9.22	nil	Bond zone between base metal and weld metal; as deposited.

Some of these materials were supplied by the Carpenter Steel Company, through W. M. Corse.

the grain boundaries as well without serious over-etching of the carbides. Etching by this procedure for carbides and grain boundaries does not result in pitting out of the inclusions. The materials listed in Table I have been chosen as examples of various types of corrosion resisting steels upon which this reagent has given satisfactory results. Many of the materials were intentionally heated to 650-675 degrees Cent. (1200-1250 degrees Fahr.) to precipitate the carbides. Figs. 1 to 5 show the results. In all cases the etching period for revealing carbides was 15 to 30 seconds and for carbides and grain boundaries, 45 to 60 seconds.

Figs. 1a and 1b show the structure of an 18-8 alloy, containing 0.06 per cent carbon, after treatment at 650 degrees Cent. (1200 degrees Fahr.) which caused practically all of the carbides to migrate to the grain boundaries. Many of the boundaries are free from carbides obviously because of the low percentage of carbon. Twins are clearly shown. Figs. 1c and 1d show the structure of a chromium-iron heated for 1 hour at 950 and 650 degrees Cent. (1740-1200 degrees Fahr.), respectively. The carbon content was far in excess of that which could be retained in solid solution in the ferrite, and

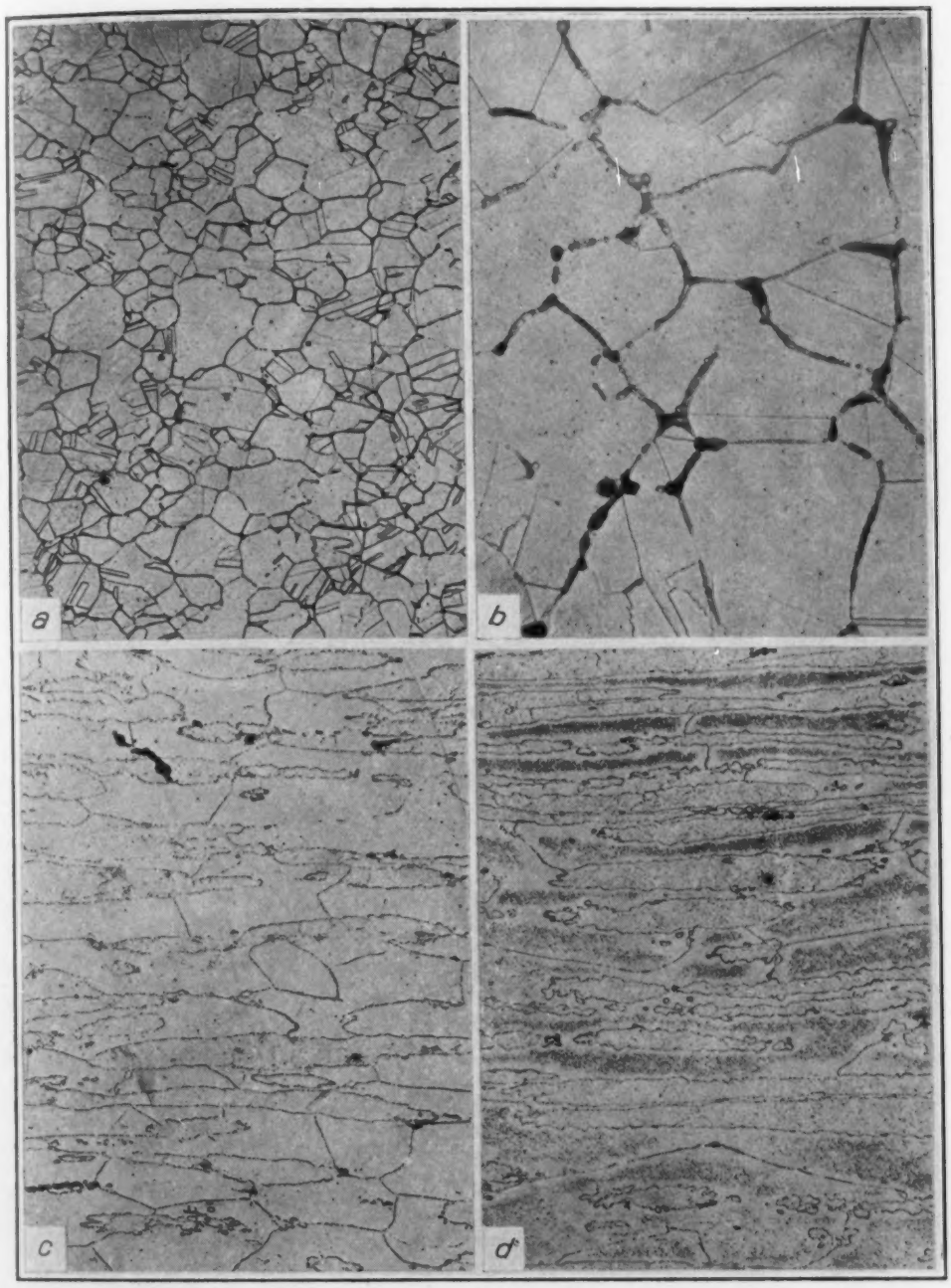


Fig. 1—Structure of 18-8, and of 17 Per Cent Chromium, Corrosion-Resisting Alloys. Etched with 10 Per Cent Oxalic Acid. (a) Specimen No. 1 (18-8). Etched for Carbides and Grain Boundaries. × 100. (b) Specimen No. 1 (18-8). Etched for Carbides and Grain Boundaries. × 500. (c) Specimen No. 7 (17 Per Cent Chromium Iron). Annealed at 950 Degrees Cent. (1740 Degrees Fahr.) for 1 Hour. Etched for Carbides and Grain Boundaries. × 100. (d) Specimen No. 7 (17 Per Cent Chromium Iron). Annealed at 650 Degrees Cent. (1200 Degrees Fahr.) for 1 Hour. Etched for Carbides and Grain Boundaries. × 100.

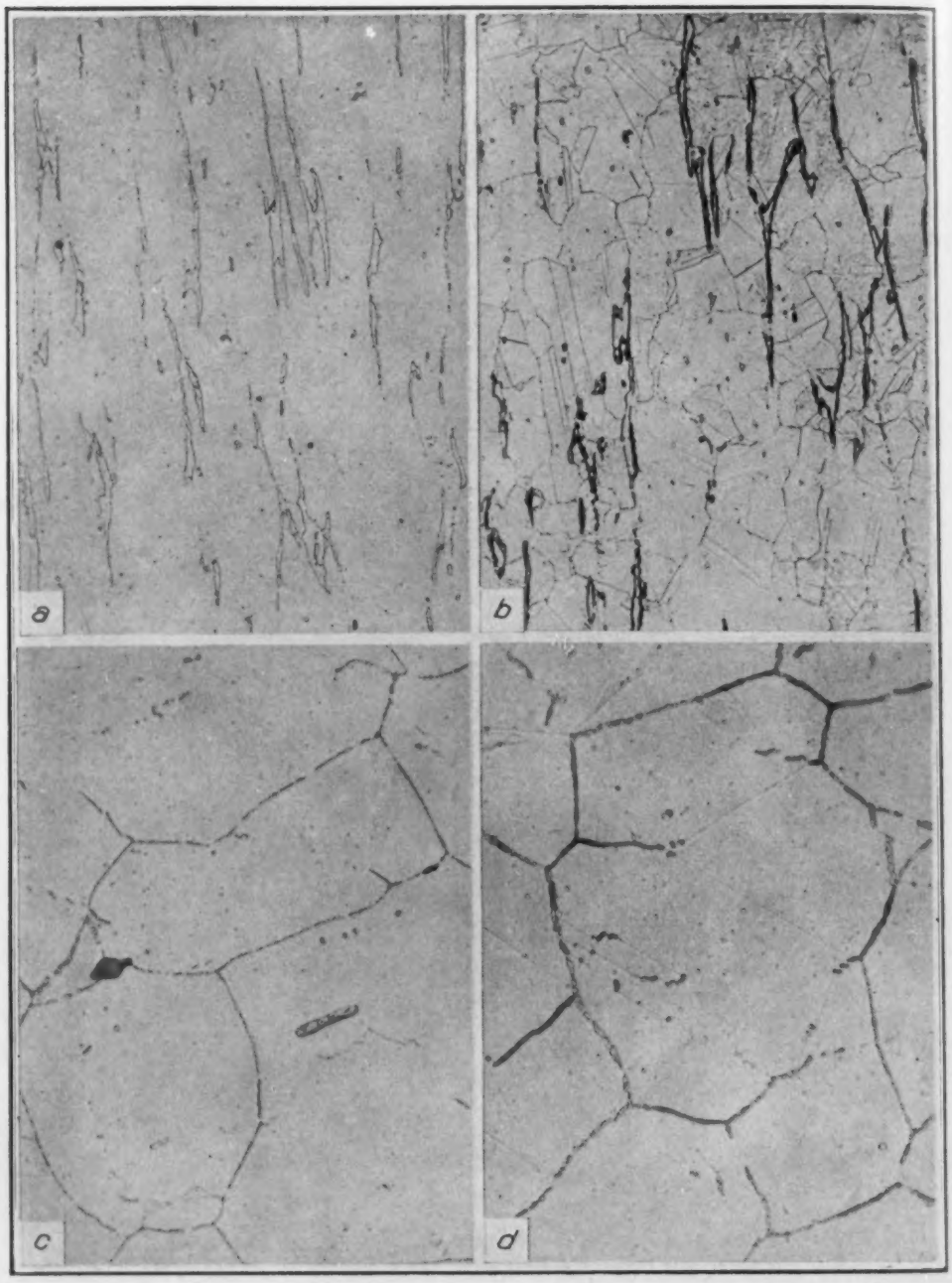


Fig. 2—Structure of 18-8 Alloys With and Without Titanium. Etched with 10 Per Cent Oxalic Acid. (a) Specimen No. 2 (18-8 Containing 0.18 Per Cent Titanium). Etched for Carbides Only. × 100. (b) Specimen No. 2 (18-8 Containing 0.18 Per Cent Titanium). Etched for Carbides and Grain Boundaries. × 100. (c) Specimen No. 4 (18-8). Etched for Carbides Only. × 500. (d) Specimen No. 4 (18-8). Etched for Carbides and Grain Boundaries. × 500.

carbide precipitation at the grain boundaries is marked. A pronounced coring effect will also be noted in the specimen heated to

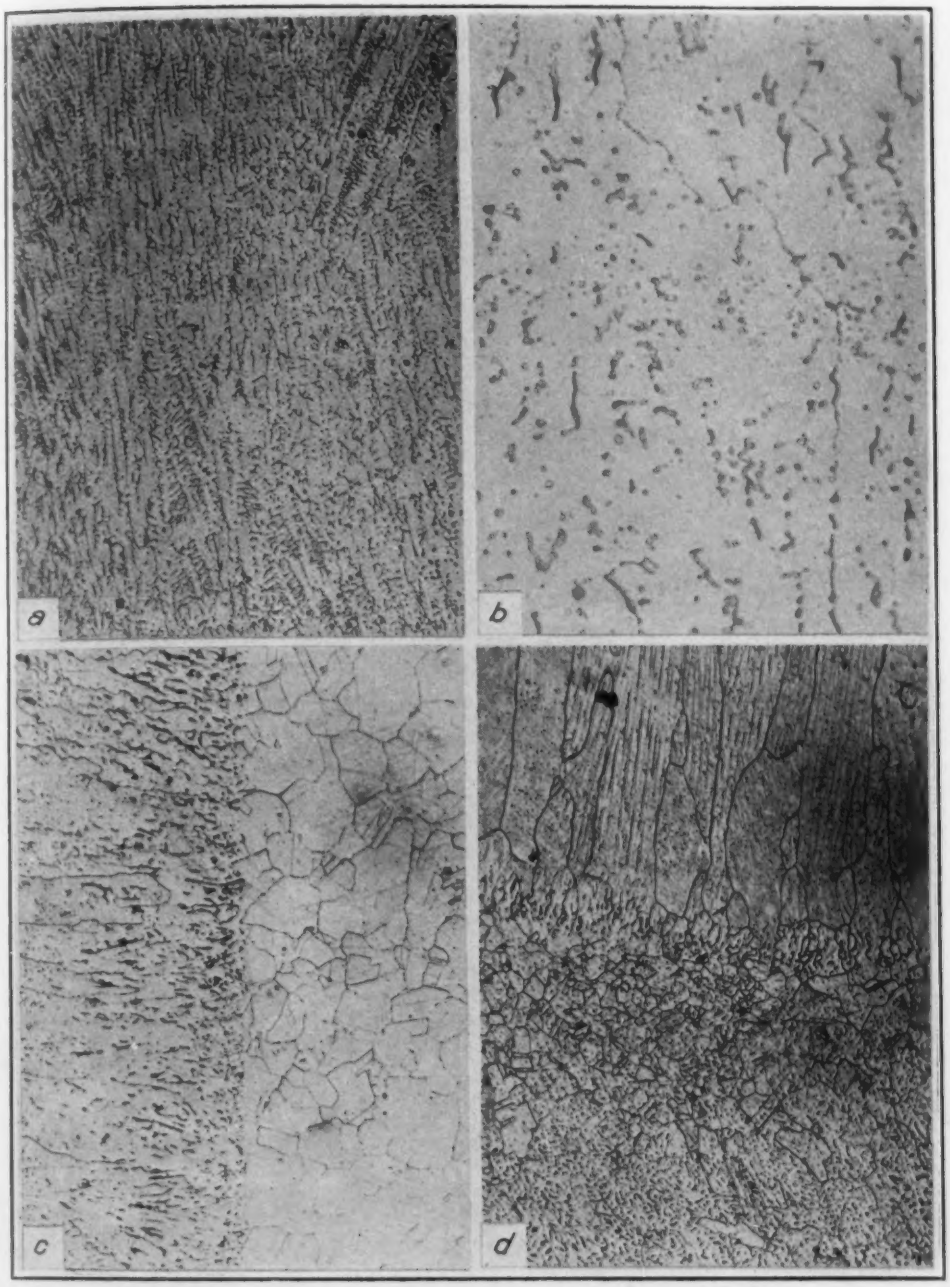


Fig. 3—Typical Structures of Welded 18-8 Alloys. Etched with 10 Per Cent Oxalic Acid. (a) Specimen No. 3. Interior of Weld Metal. Etched for Carbides Only. × 100. (b) Same as (a). × 500. (c) Specimen No. 9. Bond Zone Between 18-8 Base Metal (Right) and 18-8 Weld Metal (Left). Etched for Carbides and Grain Boundaries. × 100. (d) Specimen No. 8. Junction of Two Welding Beads in Interior of 18-8 Weld Metal. Etched for Carbides and Grain Boundaries. × 100.

650 degrees Cent. (1200 degrees Fahr.), due presumably to the slow migration of the carbides to the grain boundaries.

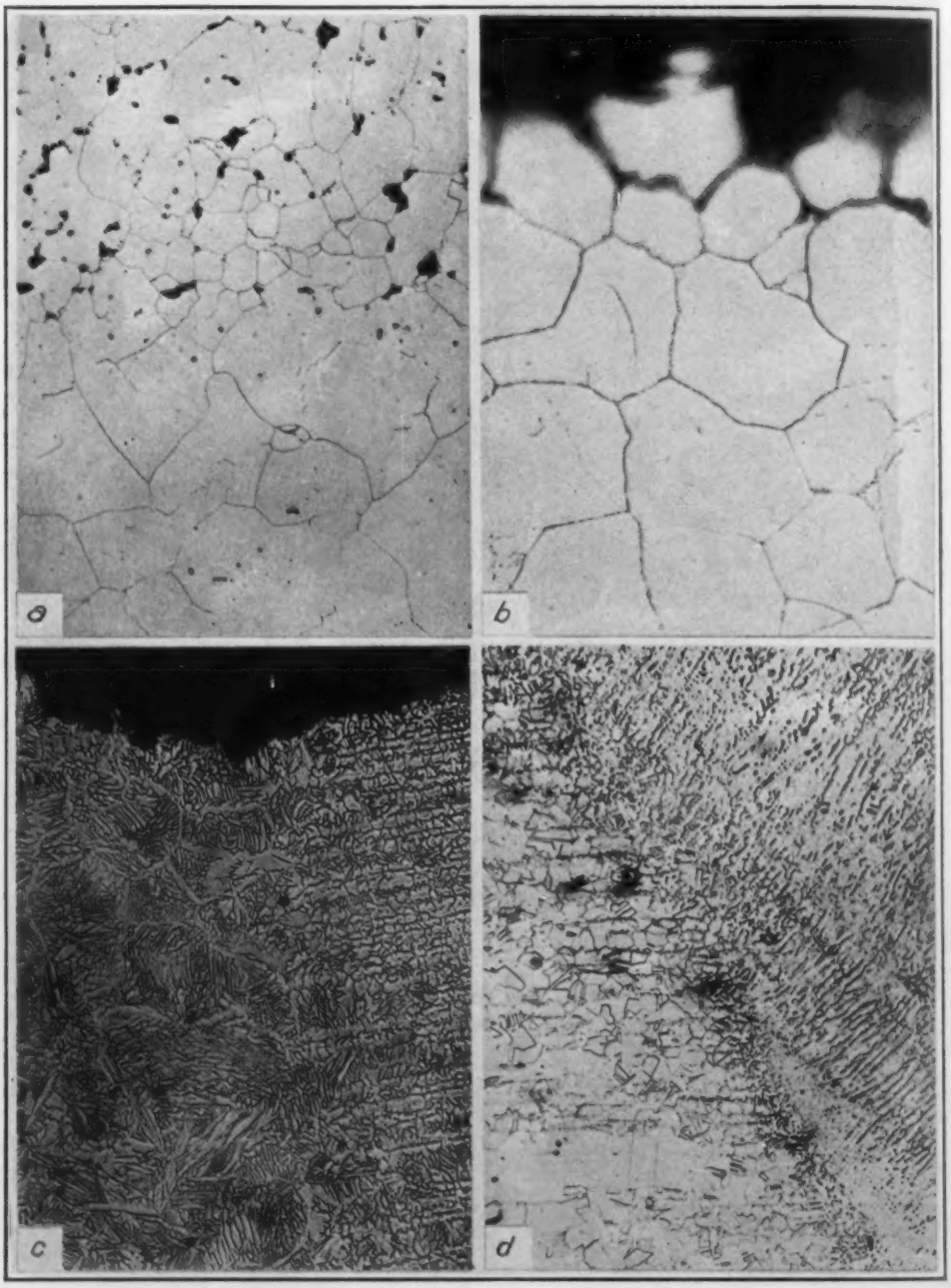


Fig. 4—Structure of Gas and Arc Welded Specimens of 18-8 Alloy and Intergranular Corrosion Attack Following Carbide Precipitation. Etched with 10 Per Cent Oxalic Acid. (a) Specimen No. 5. Interior of Weld Metal Deposited by Gas Welding. Etched for Carbides Only. × 100. (b) Specimen No. 5. Intergranular Corrosion Attack Following Carbide Precipitation at a Short Distance from the Weld Shown in (a). Etched for Carbides Only. × 500. (c) Specimen No. 6. Bond Zone Between 18-8 Base Metal Containing Titanium and Weld Metal Deposited by Gas Welding. Etched for Carbides Only. × 100. (d) Specimen No. 8. Bond Zone Between 18-8 Base Metal and 18-8 Weld Metal Deposited by Arc Welding. Etched for Carbides and Grain Boundaries. × 100.

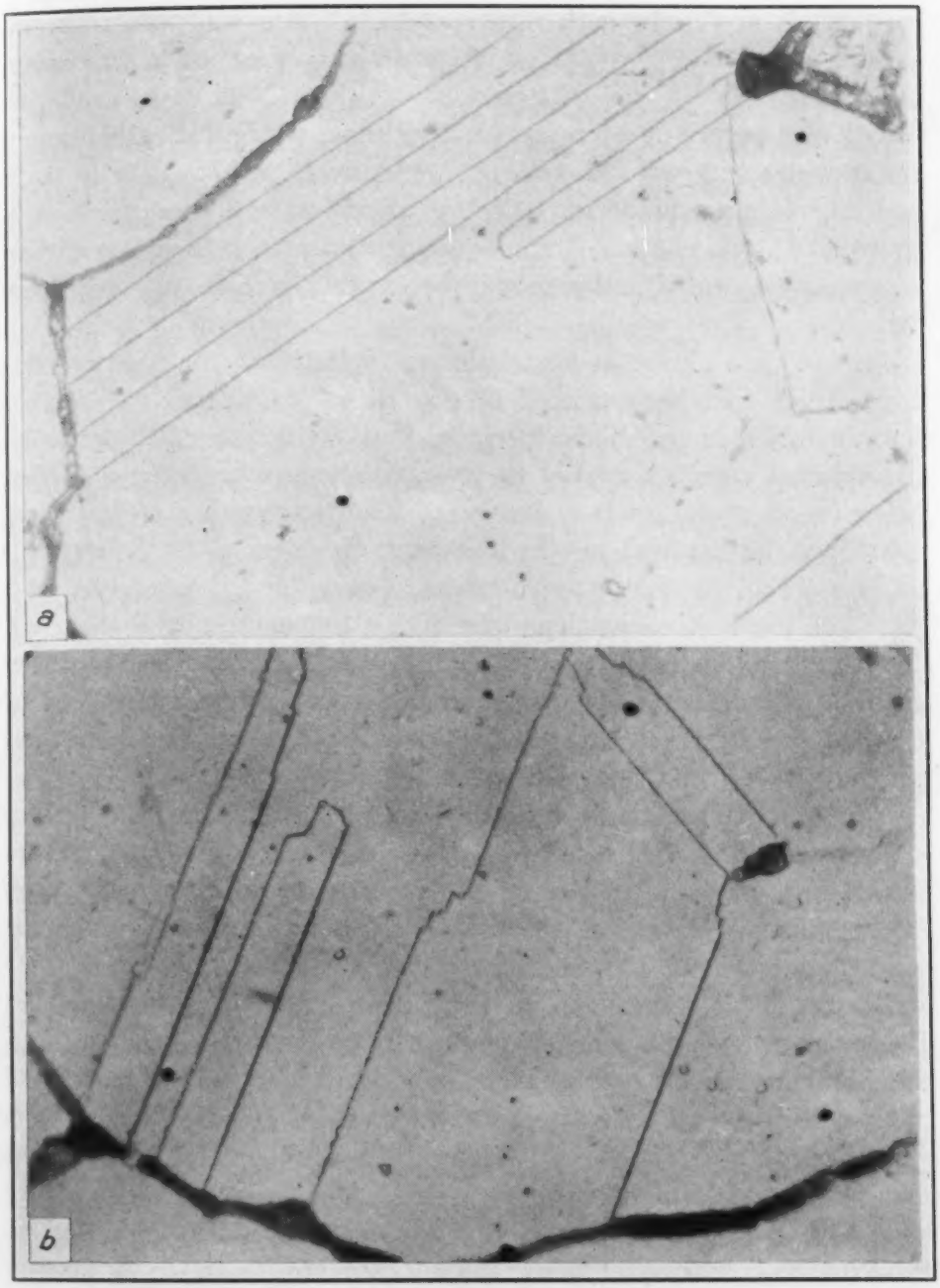


Fig. 5—Structure of 18-8 Alloy at High Magnification. Etched with 10 Per Cent Oxalic Acid. (a) Specimen No. 1. Etched for Carbides and Grain Boundaries. × 1500. (b) Specimen No. 1. Etched for Carbides and Grain Boundaries. × 1500.

The structure of an 18-8 alloy containing titanium, etched for carbides only, is shown in Fig. 2a; and in 2b, when etched to reveal grain boundaries as well. Delta ferrite outlined with precipitated

carbides is shown in both photographs. There was practically no carbide precipitation at the austenite grain boundaries in this specimen.

The structure of a low carbon 18-8 alloy, etched for carbides, and for carbides and grain boundaries, respectively, is shown in Figs. 2c and 2d. Grain boundaries with no carbide precipitation are clearly shown. This is another example which indicates that in low carbon alloys some grain boundaries may be entirely free from precipitated carbides.

Figs. 3a and 3b show carbides precipitated in the interior of a weld which had been treated at 650 degrees Cent. (1200 degrees Fahr.) for 1 hour. This specimen was etched for carbides only. Precipitated carbides appear to be distributed rather generally, few being found at the grain boundaries. The temperature to which the metal was heated was not high enough to cause general recrystallization. Fig. 3c shows the bond zone between a low carbon 18-8 plate and the weld metal deposited with a low carbon 18-8 electrode. The simultaneous revealing of base and weld metal structures makes possible a complete study of the welded zone. This is also true of Fig. 3d which shows the junction between two welding beads deposited with an 18-8 alloy electrode.

Figs. 4a and 4b show structures found in an aircraft gas-welded exhaust collector ring made of 18-8 alloy sheet. The structure shown in Fig. 4a is typical of the weld metal and Fig. 4b shows intergranular corrosion of the base metal a short distance from the weld, both specimens having been etched for carbides only. Fig. 4c shows the bond zone between metal deposited by gas welding and 18-8 base metal containing titanium. Delta ferrite is in evidence in the base metal. The bond zone between arc-deposited 18-8 weld metal and 18-8 base metal is shown in Fig. 4d.

Figs. 5a and 5b show that structures revealed by this reagent may be studied at higher magnifications. The grain boundaries contain precipitated carbides which were over-etched in the development of the structure of twins, and of boundaries containing no carbides. That this is not a serious objection can be readily seen from the photographs.

No attempt has been made, nor is it within the scope of this paper, to discuss in detail any of the structures shown or the causes for them, since the sole purpose is to discuss an etching method which may have some value.

Summary

The method is extremely simple in application, the reagent is relatively rapid in action and does not have the poisonous nor corrosive action of cyanides or mixed strong acids. An added advantage, which is quite important, lies in the freedom from staining of the specimen, both in the etching bath when the current is interrupted, and after removal from the bath. Etched specimens have been stored for as long as six months and photographed without further polishing. This is of decided advantage where it is necessary to study specimens which have been polished at some previous time.

Some application has been made of the reagent for the study of macrostructures of welded specimens. Each welding bead or layer is revealed upon etching for a period of about two minutes.

Not all of the corrosion resisting alloys can be etched by the reagent. Alloys containing selenium, in particular, are not completely etched.

This investigation is a portion of an extensive study of welding of corrosion resisting alloys conducted at this Bureau with the cooperation of L. C. Bibber, Senior Welding Engineer of the Bureau of Construction and Repair, Navy Department.

DISCUSSION

Written Discussion: By R. E. Cramer, Special Research Assistant in Engineering Materials, University of Illinois, Urbana, Illinois.

Mr. Ellinger's announcement of the oxalic acid etching reagent in "Technical News Bulletin" occurred just as the writer was starting some work on austenitic steel turbine blades, so this reagent was used extensively. Because no platinum foil or gauze was readily available in our laboratory, a piece of the austenitic steel was used for the cathode which worked quite satisfactorily. This method of etching proved very useful in showing the amount of austenite which had broken down along the grain boundaries because it left the narrow band of ferritic material containing precipitated carbides in place, with the carbides faintly outlined, while stronger acids such as 2 per cent nital dissolved away the ferritic material leaving the carbides standing out in relief. This property of the etching reagent is very useful and we are considerably indebted to Mr. Ellinger for developing the oxalic acid method of etching.

Written Discussion: By H. H. Walkup, office of inspector of naval material, Munhall, Pa.

Mr. Ellinger has shown the oxalic acid etch to be a useful etch for the 18-8 type alloys, when it is desired to etch these alloys for general structure. All the photomicrographs are said to be etched for carbides and some for

carbides and grain boundaries. The distinction between a carbide-containing grain boundary and a grain boundary, or trans-crystalline markings, is shown in Fig. 1b and 5a and 5b, the carbide-rich markings appearing the darkest. It would be interesting to know whether or not as good an etch can be obtained on fully annealed alloys of this type but containing different addition elements and having varying degrees of cold work.

The structures shown in Fig. 2a and 2b of the titanium-containing alloy are in agreement with the heat treatment given the alloy, since they indicate the alloy to be in an "unstabilized" condition; no finely globular highly dispersed carbides appearing in the photomicrograph. It would be of interest to know if finely globular highly dispersed carbides can be revealed in commercially "stabilized" titanium-bearing alloys, by the use of the oxalic acid etch.

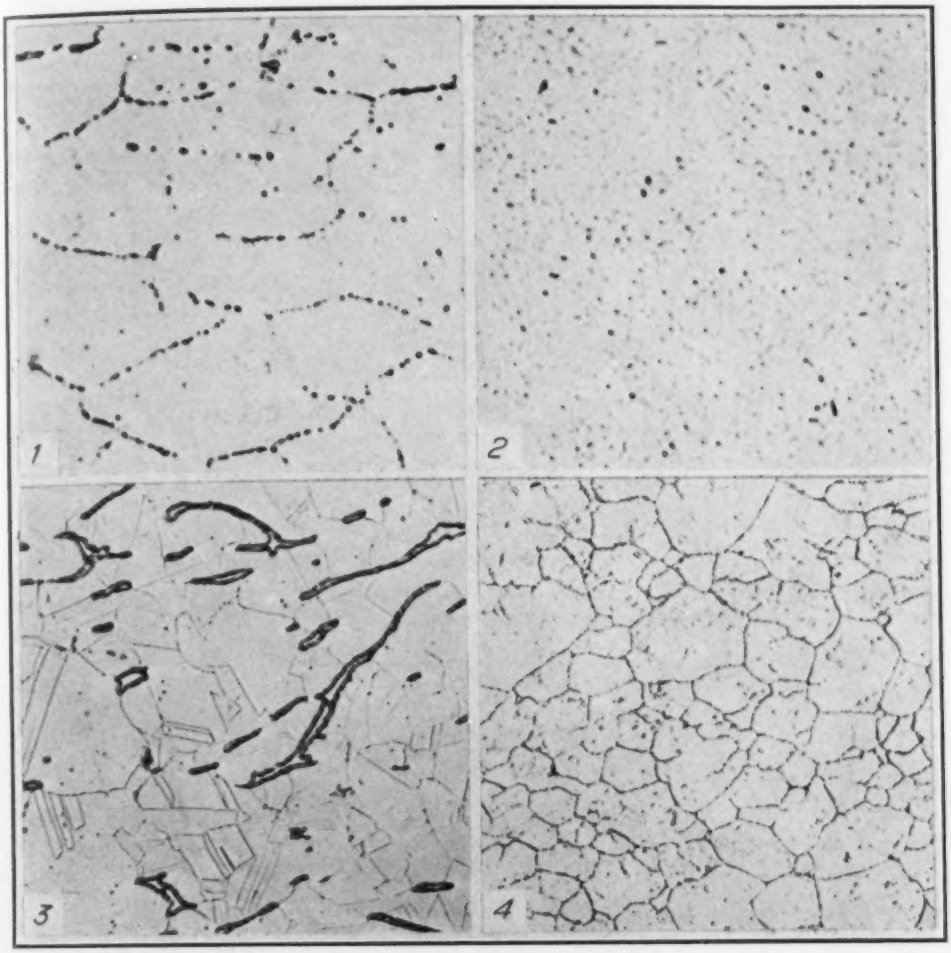
On the second page of the paper Mr. Ellinger comments on the sodium cyanide electrolytic etch by saying that it is of great value in revealing carbides, but is slow in action and has the disadvantage of not revealing grain boundaries. The first of these three notations has been demonstrated by its inclusion in Navy Department specifications after it was found to reveal structures that could be correlated with the results of the Strauss test. Also the finely globular highly dispersed carbides, which according to theory, should appear in "stabilized" titanium-bearing alloys can be revealed by this etch.

The second notation, that the etch is slow in action, is true when compared to the etching times reported by Mr. Ellinger. The conditions for the sodium cyanide etch are the same as those reported for the oxalic acid etch, except chemically pure sodium cyanide is substituted for the oxalic acid and either the platinum gauze or an 18-8 type sheet can be used as cathode. These conditions for the sodium cyanide etch were chosen after it was found they could give reproducible results when used by different laboratories. The etching time can be altered to suit the individual requirements by increasing or decreasing the current density on the polished surface of the specimen during etching.

The third notation, that the sodium cyanide etch has the disadvantage of not revealing grain boundaries, was possibly made because of not continuing the etching time long enough. The action of the sodium cyanide etch appears to be by general dissolution of the surface of the specimen; the revealed structure being a result of different rates of attack and not a result of staining. This conclusion was reached after it was found that the dark areas revealed by the etch (by oblique lighting) could be made bright by changing the focus or angle of incident light on the specimen and that the grain boundaries of a completely annealed alloy could be revealed by extending the time of etching.

When using the sodium cyanide etch on different 18-8 type alloys from different sources, the following procedure has been followed:

1. In polishing the specimen, cut the surface; do not buff it.
2. Etch for three minutes, wash in water then alcohol and dry in air. The dried specimen is then examined under the microscope for preferentially attacked areas, such as grain boundaries, dispersed carbides, delta iron, etc.
3. The appearance of the specimen is noted or a picture is taken and the specimen is again etched for two minutes and the above procedure repeated.
4. The operations of re-etching and examining are repeated if desired,



Photomicrographs of Structures Obtained with the Sodium Cyanide Electrolytic Etch.
Fig. 1—Alloy 1, 18-8 Type Alloy with Area Affected by Welding. × 500.
Fig. 2—Alloy 2, 18-8 Type Alloy Containing Titanium and "Stabilized." × 500.
Fig. 3—Alloy 3, 18-8 Type Alloy Deeply Etched, Revealing Two Phases.
Fig. 4—Alloy 4, 18-8 Type Alloy "Sensitized."

until those grain boundaries which have not appeared in earlier etches appear as halftones. (See Mr. Ellinger's paper, Fig. 5.)

Usually item four of this procedure is only included when the polishing technique of the specimen is questioned and the specimen shows freedom from carbides.

The sodium cyanide etch, as given here, is not for revealing general structure but to reveal structure that can be correlated with the results of the Strauss test. When it is desired to reveal general structure a selection from the following etches is used: (1) oxalic acid, (2) perchloric acid, (3) nitric acid, (4) hydrochloric acid in alcohol or (5) Vilella's. The first four are electrolytic while the fifth is simple immersion.

Written Discussion: By H. P. Munger and C. D. Foulke, American Rolling Mill Co., Middletown, Ohio.

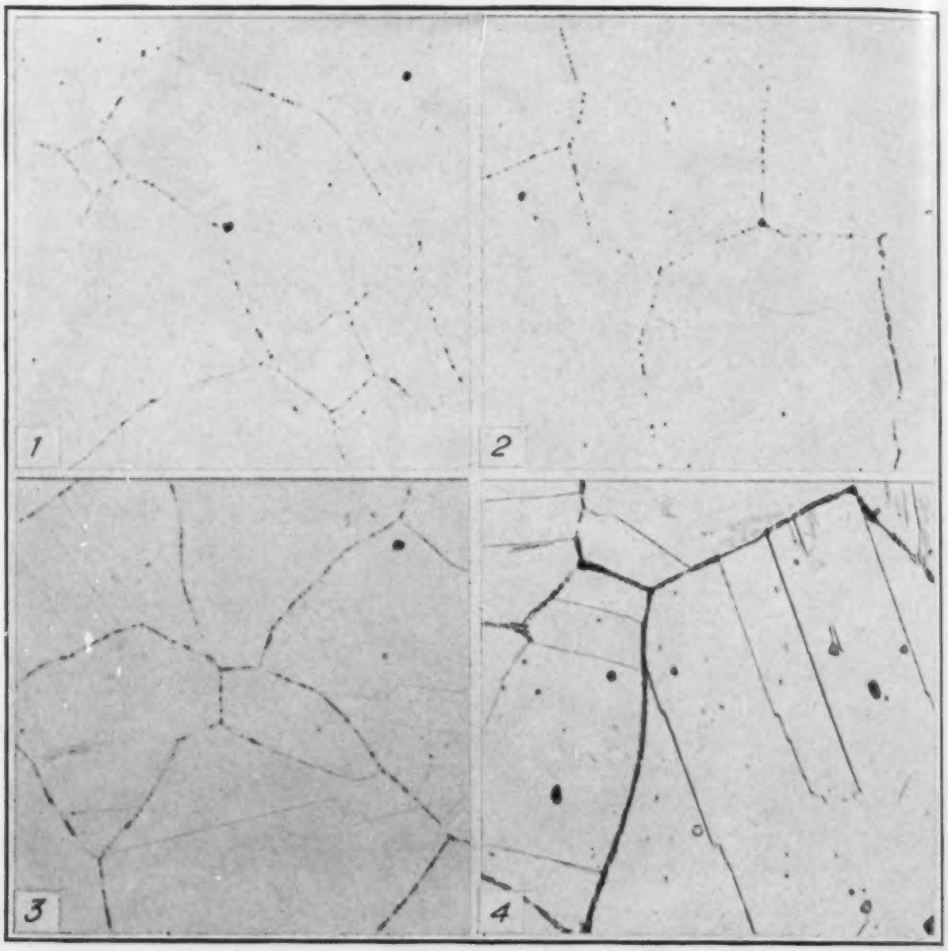


Fig. 1—Austenitic Chromium-Nickel Steel Etched for 5 Minutes in Sodium Cyanide. × 500.
Fig. 2—Same as Fig. 1 After Etching an Additional 10 Minutes in Sodium Cyanide. × 500.
Fig. 3—Austenitic Chromium-Nickel Steel Etched for 15 Seconds in Oxalic Acid. × 500.
Fig. 4—Same as Fig. 3 After Etching an Additional 30 Seconds in Oxalic Acid. × 500.

The author is to be complimented for his contribution to the microscopic examination of corrosion resistant alloys. Oxalic acid would appear to be a satisfactory reagent for revealing grain structures of stainless alloys, especially of welded materials. We are not in complete agreement, however, as to the merits of some characteristics of the reagent mentioned by the author.

Considerable emphasis is placed upon the fact that oxalic acid is a dual etching medium capable of revealing both carbides and grain structures. This would, no doubt, be of considerable value in some cases, however, it may lead to confusion in the identification of small amounts of carbide in the grain boundaries. It is generally conceded at the present time that susceptibility of austenitic chromium-nickel steels to failure due to intergranular corrosion is associated with precipitation of carbides in the grain boundary. In producing

material to be used in the most exacting services where intergranular deterioration is a major factor, it is often imperative to detect slight traces of carbides. For this purpose it is desirable to etch the specimen with a reagent which is not only specific in its action on carbides but only very mildly progressive as well. That sodium cyanide incorporates these desirable characteristics in contrast to oxalic acid is shown by Figs. 1 to 4 inclusive. Figs. 1 and 2, etched with sodium cyanide for 5 and 15 minutes, respectively, show this reagent to be quite specific, within reasonable lengths of time, in its action on carbides and to be only very mildly progressive. The results of etching this same sample with oxalic acid for 15 and 45 seconds are shown in Figs. 3 and 4, respectively. The dual etching of this reagent and its progressive action is revealed. Because of this progressive action there may be some question as to what length of time should be used to develop the carbide structure. Although 15 to 30 seconds is the time suggested for etching carbides, a shorter time may show an apparently lesser amount of carbide and a longer time an apparently greater amount of carbide, this action continuing until the entire structure is developed.

In view of these facts, we do not agree that the failure of sodium cyanide to reveal grain structures is a disadvantage, but on the contrary, a distinct advantage.

In closing we wish to reiterate our statements that oxalic acid appears to be a satisfactory etch for revealing grain structures when used for such. The dual and progressive etching action of this reagent, however, may lead to confusion in an estimation of the true amounts of carbide present.

Written Discussion: By W. B. Arness, Rustless Iron Corp. of America, Baltimore, Maryland.

Mr. Ellinger is to be sincerely commended for his contribution to the literature of stainless steels, and I join all users and producers of stainless steels in thanking him. Heretofore we have had several excellent papers which discuss one or another aspect of carbide precipitation, but this is the first which is directed primarily toward giving assistance to practical metallurgists, who are not specialists in the stainless field, in the interpretation of 18-8 structures containing carbides.

The author's subject is a controversial one, and no doubt he expected some differences of opinion to be expressed. The more credit to him because, at this early stage the subject is not cut and dried, and what he now presents for public scrutiny and testing will advance the art just as surely whether or not future experience confirms his views.

Our laboratory was probably the first to test and adopt NaCN electrolytic etching for interpretation of 18-8 structures containing carbides. Mr. S. P. Watkins of our metallurgical staff, found mention of this method in delving through the literature, tried it, and has successfully developed it into a most useful tool. As a result, we are advocates of the use of the NaCN reagent for studying carbide precipitation, and take issue with Mr. Ellinger in his preference for oxalic acid.

I shall not take time here to discuss the NaCN test in detail, or to describe procedure for using it, as a paper will soon be published by the A.S.M. devoted entirely to this subject.

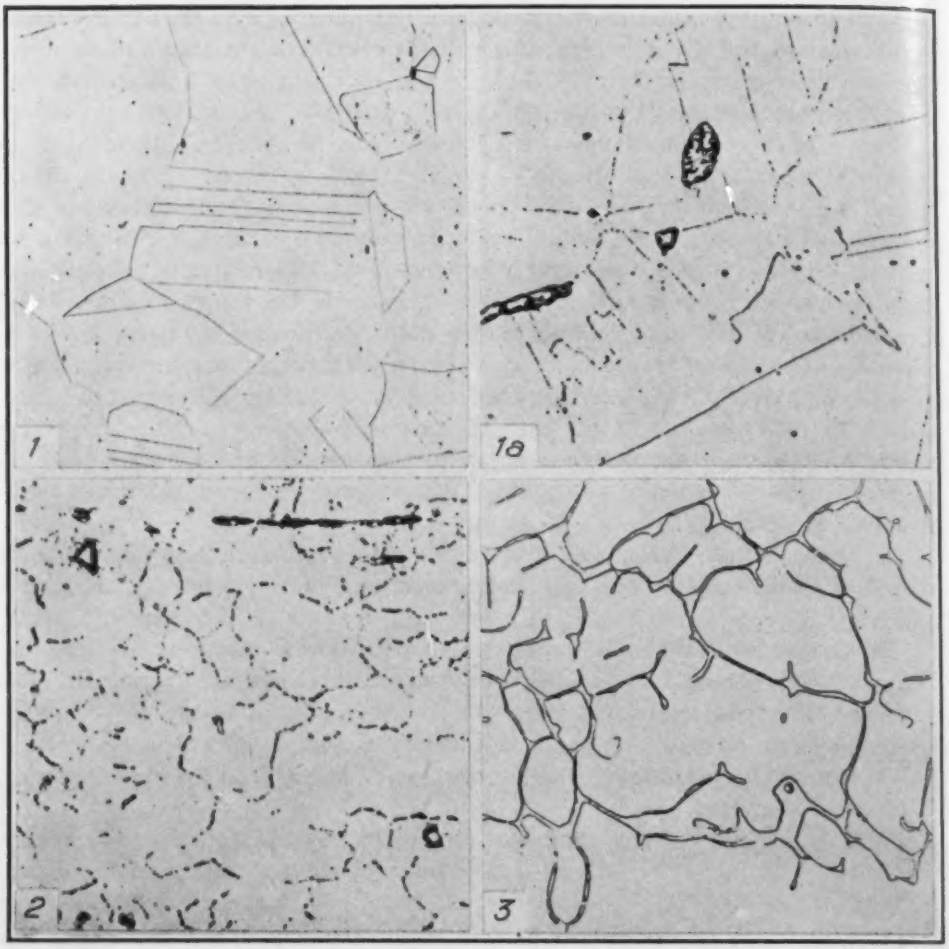


Fig. 1—Steel Containing C 0.07, Cr 19.8, Ni 9.4 Annealed. No Precipitated Carbides. Etched Electrolytically in Oxalic Acid. × 500.

Fig. 1a—Steel Containing C 0.06, Cr 19.8, Ni. 8.9 Annealed Plus 1200 Degrees Fahr. Carbides Precipitated in Boundaries. Etched Electrolytically in Sodium Cyanide. × 500.

Fig. 2—Steel Containing C 0.067, Cr 18.89, Ni 9.23, Ti 0.27. Square ⅞ Inch "As Received" (187 BH) Plus 1250 Degrees Fahr. 10 Minutes. Air Cooled. Globularized Carbide Network. Delta Iron Streak at Top. Sodium Cyanide Etch. × 500.

Fig. 3—Steel Containing C 0.05, Cr 18.8, Ni 8.9. Test Ingot Cast and Quenched. Carbides not Precipitated. Probably Ferrite Pools in Austenitic Matrix. Sodium Cyanide Etch. × 500.

The author has chosen for his reagent one that admittedly reveals both carbides and austenite. On this basis alone we would question its selectiveness. Using it, appeals to us somewhat like making a chemical analysis for one element with a reagent which precipitates the desired element, plus one or two others.

We also experienced some difficulty in following the author's interpretation of results, especially his illustrations at 100 diameters. This low magnification has given us no satisfaction in our studies of carbide precipitation.

In Fig. 1 and Fig. 2 of this discussion are shown two structures. One is an annealed structure free of carbides, which has been etched with oxalic acid;

the other, subjected to carbide precipitation treatment and etched with sodium cyanide. Note the similarity in appearance of the two photographs. In considering such results as these, we cannot escape the impression that use of the oxalic acid might result in creating suspicion of carbide precipitation in structures which are in fact free of it.

Referring specifically to Mr. Ellinger's Fig. 2a, illustrating an 18-8 titanium structure which has been subjected to a short carbide precipitation treatment, we are inclined to suspect that carbides should be present. The rates of precipitation in all 18-8 steels are not necessarily identical, and it appears that adding titanium may change the temperature for maximum rate of precipitation, but it is well known that the 18-8 titanium grade is subject to carbide precipitation, and that its resistance to intergranular disintegration does not depend upon the absence of precipitation, but is instead a function of the distribution of carbides and perhaps of their composition. The sodium cyanide etch test at about × 500 reveals the presence of precipitated carbides in the 18-8 titanium steel after welding or after carbide precipitation heat treatment, as may be seen in our Fig. 2.

In Fig. 3a of Mr. Ellinger's paper he implies that the dark constituent in the "as cast" structure is largely precipitated carbides. Here again, the low magnification makes it difficult to interpret results. Our interpretation of his Figs. 3a and 3b is that most of the dark constituent revealed is ferrite. Perhaps carbides are precipitated in the boundaries of the ferrite and in this sense his photographs may be considered to reveal carbides, yet they do not necessarily represent carbide precipitation of a type which is significant of the subsequent corrosion behavior of the material. Our own Fig. 3 shows this same type of cast structure after severe quenching. Carbide precipitation did not take place in this sample, because it was immediately quenched after casting, before reaching the carbide precipitation temperature range. The clearly outlined constituent occurring generally in the boundaries of the primary crystal is probably delta ferrite. This unusual effect might be slightly confusing if it were not that the special character of this specimen is known. The dark lines are not likely in this case to be a carbide segregate or precipitate. On the contrary they are probably the result of differential etching at the boundaries between ferrite and austenite.

In the cast structure we do not ordinarily see typical carbide precipitation until after the material has been annealed. Our Fig. 4 shows this effect. Here the specimen was heated to 1950 degrees Fahr. or thereabouts, quenched, and then subjected to a carbide precipitation treatment. Grain boundaries may be seen faintly outlined with precipitated carbides.

In contrast to the oxalic acid reagent, sodium cyanide does not etch austenitic grain boundaries until the time of etching is inordinately prolonged. Our Figs. 5 and 6 illustrate typical results. In Fig. 5 the result is clear, and precludes error in interpretation. Even though the prior history of the sample were entirely unknown, it could be confidently predicted that the material had been annealed to preserve all carbides in solution, and that no subsequent hot or cold treatments had precipitated any. If there is some doubt whether the specimen has been etched sufficiently long, increasing the etching time three or four times as long as is required, introduces no effects which will confuse

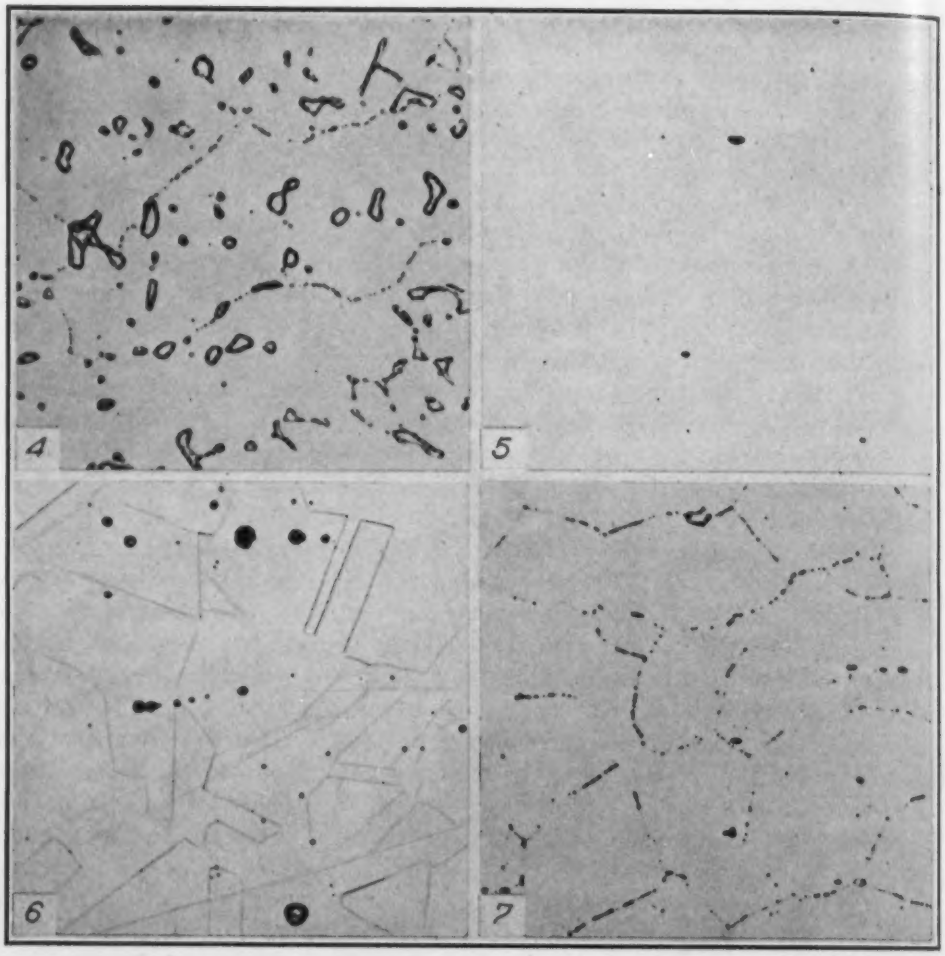


Fig. 4—Steel Containing C 0.05, Cr 20.0, Ni 9.7. Cast Structure Annealed Plus 1250 Degrees Fahr. Ferrite Pools and Some Precipitated Carbides. Sodium Cyanide Etch. × 500.

Fig. 5—Steel Containing C 0.05, Cr 17.8, Ni 9.3. Annealed, No Carbides. Sodium Cyanide Etch. 5 Minutes. × 500.

Fig 6—Steel Containing C 0.05, Cr 17.8, Ni 9.3. Annealed, No Carbides. Grossly Over-etched. Sodium Cyanide Etch 30 Minutes. × 500.

Fig. 7—Steel Containing C 0.06, Cr 19.4, Ni, 9.7. Annealed Plus 1200 Degrees Fahr. Usual Appearance of Carbides in Low Carbon 18-8 Steel when Precipitation Treatment is Short. Sodium Cyanide Etch. × 500.

the result. It is not until etching has been prolonged well in excess of 15 minutes, depending somewhat upon current density in the solution, that the sodium cyanide etch reveals constituents other than carbides. In the case of our Fig. 6, 30 minutes etching time was required before austenite was revealed.

Our last photograph, Fig. 7, illustrates the typical appearance of precipitated carbides as revealed by the sodium cyanide etch. The carbon content of this sample was low, and the treatment was not prolonged, and consequently carbides are neither pronounced nor continuous. Nevertheless, they are clearly in evidence, and plainly indicate the sensitiveness of the test.

We do not question Mr. Ellinger's ability to use oxalic acid for studying carbides. No doubt, in his own laboratory he is able to control the etching technique so as to be reasonably sure of his results. We believe we could use it too, but after trying them both, we much prefer the sodium cyanide solution. I think, in concluding, attention should be drawn to the excellence of oxalic acid as a reagent for studying austenite structures. For many special steels, differing somewhat from the familiar 18-8 composition, we are enabled to get a better definition of austenite and to more clearly see the effects upon the structure of various hot and cold treatments through its use than by any other reagent. For such uses we heartily endorse oxalic acid.

Author's Closure

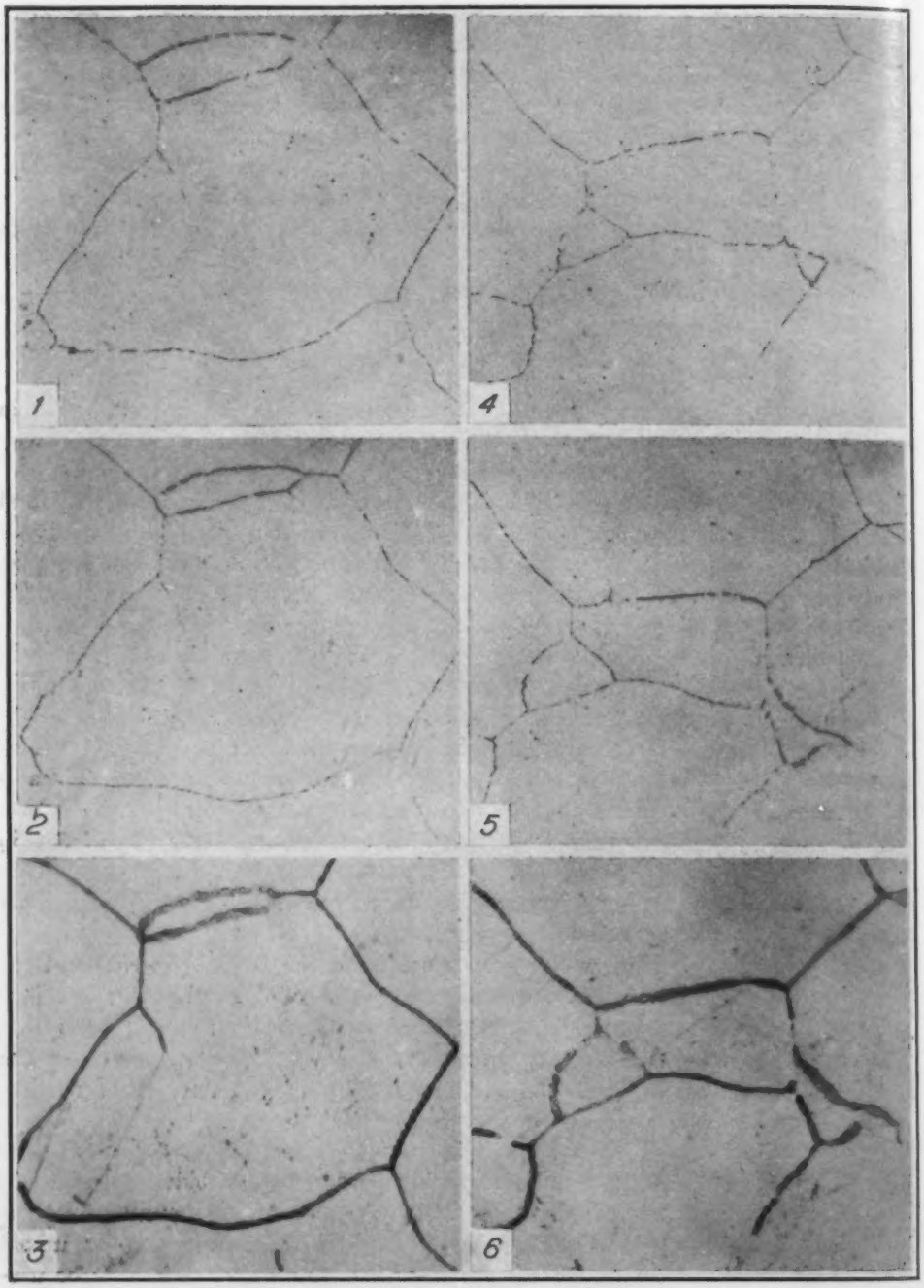
The author appreciates the discussion presented and the interest taken in the subject. That some aspects of the subject are highly controversial is well known by all who deal in this particular field.

From the discussion it would appear that there were two distinct and definite trends of thought. There is no question as to the etching quality of the reagent for general structural details, but differences of opinion exist as to the use of the reagent for the etching of carbides. Some believe that the dual effect of etching for carbides and other structural features is a disadvantage, and others, that it is an advantage. This is probably to be expected on account of the controversial nature of the situation, and the conclusions depend entirely upon what the investigator wishes to study.

For the purpose of studying carbides, to the exclusion of most other features, as in inspection under specification and for possible rejection of material where carbides are precipitated in a continuous network, a reagent such as sodium cyanide which reveals carbides only, may be suitable. However, in other cases where it is desirable to study carbides in relation to other structural features such as grain boundaries, twins, etc., then the etching characteristics of oxalic acid are to be preferred.

This was the problem which confronted us in the study of welds and for which purpose the oxalic acid reagent was developed. Incidentally it might be noted here that in the development of the reagent, sodium cyanide was used as a control to determine whether or not carbides were present. Many of the specimens shown in the body of the paper were etched first with cyanide, studied, then repolished and etched with oxalic acid.

Early in the study of welding corrosion-resisting alloys in which the writer is engaged, sodium cyanide was used to show carbide precipitation. Then it was desired to etch further to show the relationship between carbides and grain boundaries, twins, inclusions, etc. With a reagent such as mixed acids in glycerol, in many cases the specimen was so badly pitted as to be useless for study. Furthermore as was pointed out in the paper, weld metal and base metal do not etch at the same rates and again difficulties were encountered. For these reasons it became necessary to find some other etching reagent to show these features and the use of oxalic acid was found to be suitable. A specimen could be etched for ten or fifteen seconds with oxalic acid, studied under the microscope, and then etched further to develop other details with-



Figs 1-6—Structure of 18-8 Alloy Etched with Sodium Cyanide and with Oxalic Acid.
Fig. 1—Specimen No. 4. Etched 5 Minutes with Sodium Cyanide. × 500.
Fig. 2—Same Area as 1 After Repolishing, Etched 15 Seconds with Oxalic Acid. × 500.
Fig. 3—Same Area as 1 and 2, Etched 60 Seconds with Oxalic Acid. × 500.
Fig. 4—Specimen No. 4. Etched 5 Minutes with Sodium Cyanide. × 500.
Fig. 5—Same Area as 4, After Repolishing, Etched 15 Seconds with Oxalic Acid. × 500.
Fig. 6—Same Area as 4 and 5, Etched 60 Seconds with Oxalic Acid. × 500.

out seriously interfering with any other structural feature. In this way, more could be learned about weld and base metals, bond zones and carbides than could be learned by etching with sodium cyanide for carbides and then with some other reagent for other details.

It was not the purpose of this paper to advocate the replacing of any existing reagent by oxalic acid, for each reagent usually has its own peculiar advantages and field of usefulness, but it was desired to augment those already in use by one which appears to give slightly better results for certain applications. It is of interest, in this connection, to present here photographs of a low carbon 18-8 alloy, on which identical locations were etched with sodium cyanide and then with oxalic acid to show some of the relative merits of the reagents.

Fig. 1 and Fig. 4 show two locations etched for 5 minutes with sodium cyanide. Carbides are shown at the grain boundaries. Fig. 2 and Fig. 5, respectively, show the same identical locations after repolishing, etched 15 seconds with oxalic acid. A close study will show that all of the features revealed by sodium cyanide etching are also revealed by etching with oxalic acid. By stopping the etching at this time, no further details not shown by sodium cyanide are revealed. Fig. 3 and Fig. 6 show the same locations etched with oxalic acid for a total period of 60 seconds. Here the carbides are slightly over-etched but their relationship to grain boundaries and twins is clearly indicated. These photographs illustrate clearly that under proper control, oxalic acid can be used to study carbides in the laboratory just as well as sodium cyanide. It may also be noted here that reducing the amount of current used slows down the etching reaction materially and considerably better control can be obtained.

A DILATOMETRIC STUDY OF THE ALPHA-GAMMA TRANSFORMATION IN HIGH PURITY IRON

By C. Wells, R. A. Ackley and R. F. Mehl

Abstract

A dilatometric study has been made of the alpha-gamma transformation in high purity iron, using a newly developed high precision recording differential dilatometer. Approximately sixty heating and cooling dilatation curves have been made of hydrogen purified Armco iron, electrolytic iron, and carbonyl iron. Chemical and spectroscopic analyses of carbonyl iron are given. By close attention to thermometric requirements, and by proper interpretation of the dilatometric curves, it was possible to fix the temperature of the alpha-gamma transformation at 909.5 ± 1 degrees Cent. (1669 degrees Fahr.). Thermal analysis curves were obtained simultaneously and proved of value. Observations on the effects of heterogeneity, on anomalous length changes, on degrees of undercooling and superheating, and on the speed of this transformation are reported.

Introduction

THE purpose of this investigation was to prepare high purity iron and to study its behavior at the alpha-gamma transformation point in a precision recording differential dilatometer, using carefully controlled and constant rates of heating and cooling of ⅛, ½ and 2 degrees Cent. per minute, respectively, in order to determine as precisely as possible the temperature of the A_3 transformation and the effect of heating and cooling rates on the temperature of the Ac_3 and Ar_3 transformations.

Hundreds of determinations have been made on the A_3 temperature in "pure" iron.[1] The older values are of uncertain merit chiefly

[1]The bibliography assembled by G. K. Burgess and J. J. Crowe, "The Critical Ranges A_2 and A_3 of Pure Iron," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 47, 1913, p. 665, lists sixty papers on this subject. The recent summary made by the members of the metallurgical staff of the Bureau of Standards, shortly to appear as an "Alloys of Iron Monograph," is quite up to date.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. Of the authors, C. Wells and R. A. Ackley are associated with the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, and R. F. Mehl is Director of Metals Research Laboratory, and Professor of Metallurgy, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 1, 1935.

because of the lack of complete analytical data on the irons used, but even among modern data wide discrepancies exist. The simultaneous development in this laboratory of methods to prepare high purity iron and of a high precision dilatometer offered an opportunity to contribute new data on this subject.

After considering the enormous amount of A_3 data available up to 1913, much of which were contradictory, Howe[2] concluded that the A_3 temperature in pure iron is about 917 degrees Cent. (1683 degrees Fahr.). In 1913 Burgess and Crowe[3] published the results of a very careful investigation of the A_3 and A_2 transformations in about 12 high purity electrolytic irons, reported to contain 99.96 to 99.98 per cent iron and 0.003 to 0.009 per cent carbon. More than 50 tests were made in this investigation and there can be little doubt that up to 1913 it was the most thorough and accurate investigation of the A_2 and A_3 critical ranges in high purity irons. These workers used the thermal method to determine the alpha-gamma transformation temperatures at various heating and cooling rates ranging from 2 to 10 degrees Cent. per minute. The Ac_3 and Ar_3 temperatures at zero rate (909 $\pm$ 1 degree Cent. and 898 $\pm$ 2 degrees Cent. respectively) were then obtained by extrapolation. Since the temperature of the alpha-gamma transformation is less affected by the rate of heating than the rate of cooling the Ac_3 figure 909 degrees Cent. (1669 degrees Fahr.), assumed at zero rate, should be much closer to the A_3 equilibrium temperature than the Ar_3 figure 898 degrees Cent. (1648 degrees Fahr.). The difference of approximately 10 degrees Cent. between the Ac_3 and Ar_3 temperatures at zero rate is surprising, however, and is not in accord with our conceptions of transformations of this sort.

In 1914 Benedicks[4] determined the Ac_3 and Ar_3 temperatures dilatometrically using a high purity electrolytic iron reported to be 99.97 per cent iron with 0.008 per cent carbon. Benedicks used a sensitive differential dilatometer and obtained excellent data, indicating that the dilatometric method is one of the best for a precise determination of the A_3 temperature in iron. Benedicks' results showed the Ac_3 temperature at a heating rate of 2 to 5 degrees Cent. per minute to be between 907 and 911 degrees Cent. (1665-1672

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[2]H. M. Howe, Discussion of the Existing Data as to the Position of Ac_3, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 47, 1913, p. 611.

[3]Ref. 1.

[4]C. Benedicks, "Experiments on Allotropy of Iron; Behavior of Ferro-Magnetic Mixtures; Dilatation of Pure Iron," *Journal*, Iron and Steel Institute, Vol. 89, 1914, p. 407.

degrees Fahr.) which is in agreement with the results obtained by Burgess and Crowe.

Esser[5] in 1927 published a number of excellent dilatometric curves which show a spread of only 2 to 3 degrees Cent. between the beginning and the end of both the Ac_3 and Ar_3 transformations. Esser's curves showed an Ac_3 temperature of about 905 degrees Cent. (1661 degrees Fahr.) and an Ar_3 temperature of about 900 degrees Cent. (1652 degrees Fahr.).

In 1928 Sato[6] made a determination of the A_3 temperature in a high purity iron, which he claimed to contain only 0.008 per cent carbon, 0.006 per cent phosphorus, 0.007 per cent sulphur, and no manganese, silicon, or copper; he reported a value of 903 degrees Cent. (1657 degrees Fahr.). The dilatometric method was used by Sato and the Ac_3 and Ar_3 temperatures determined at various rates of heating and cooling, and the A_3 temperature by extrapolation to zero rate. Sato's dilatometric curves, unlike those of Esser, indicate considerable temperature spread during the alpha-gamma transformation both on heating and cooling. It may be assumed that much of this spread was caused by instrumental or thermometric discrepancies, and perhaps to some extent by the presence of 0.008 per cent carbon. Like other investigators, Sato assumed that the temperatures at the beginning of the Ac_3 contraction on heating and the Ar_3 expansion on cooling should be considered the Ac_3 and Ar_3 temperatures respectively. No doubt in many cases this is not justified and has led to the recording of low A_3 data. As indicated in one of Sato's curves the temperature limits at the beginning and end of the Ac_3 transformation are 904 and 914 degrees Cent. (1659-1677 degrees Fahr.), when the rate of heating is ½ degree Cent. per minute. The average temperature is 909 degrees Cent. (1668 degrees Fahr.) and is in agreement with the results of Burgess and Crowe[7] and Benedicks.[8] This spread is much too great, probably originating in a considerable temperature gradient in the specimens under observation. The low A_3 (903 degrees Cent.) reported by Sato may also have been caused in part by the interpretation of the dilatometric curves adopted and in part by the presence of 0.008

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[5]H. Esser, "Dilatometrische u. Magnetische Untersuchungen auf reinen Eisen u. Eisen Kohlenstoff legierungen," *Stahl und Eisen*, Vol. 47, 1927, p. 337.

[6]T. Sato, "The Critical Points of Pure Carbon Steels," Tohoku Imperial University Technical Reports, Vol. 8, 1928-1929, p. 27.

[7]Ref. 1.

[8]Ref. 4.

per cent carbon which lowers the A_3 in iron by 3 or 4 degrees Cent.

In recent years hydrogen-treated high purity irons have been prepared which are considered to be much purer than those studied previously. Recent investigators[9] report that iron of this sort possesses an unusually high A_3 transformation temperature (up to about 930 degrees Cent.). Austin and Pierce report that specimens of iron of apparently similar high purity may have considerably different alpha-gamma transformation temperatures.

Preparation and Analysis of High Purity Iron

Carbonyl iron was selected from a number of varieties of iron which had been examined spectroscopically as the most suitable for the preparation of high purity iron by hydrogen purification. The impurities present in the largest amounts in carbonyl iron as received are oxygen and carbon, and these are easily removed by heating in hydrogen for a sufficiently long time at a sufficiently high temperature.

To overcome the possibility of introducing impurities into the carbonyl iron during the hydrogen treatment, the iron sheet specimens were mounted on previously purified carbonyl iron supports which rested on pieces of chemically pure magnesia. This magnesia served to avoid direct contact between the hydrogen-purified Armco iron tube in which the samples were held and the specimens of carbonyl iron. The carbonyl iron sheets were approximately 10 by 3 by 0.125 inches in size; these sheet specimens were appropriately spaced so as to expose a large surface area to the hydrogen during purification. The hydrogen was passed through a heated platinized asbestos combustion chamber, a sulphuric acid drying tower, and an activated alumina drying tower, and thence to the charge. Chemical and spectroscopic analysis of hydrogen purified carbonyl iron after various treatments are given in Table I.

Methods Used

The precision recording differential dilatometer used in this investigation will shortly be described in detail elsewhere; only the general features of the equipment need be described here.

[9] F. R. Hensel, Discussion of a paper by T. D. Yensen and N. A. Ziegler, *Transactions*, Iron and Steel Division, American Institute of Mining and Metallurgical Engineers, Vol. 95, 1931, p. 322; F. R. Hensel and E. I. Larsen, "A Note on the A_3 Point of Highly Purified Iron," *Metals and Alloys*, Vol. 4, 1933, p. 37; J. B. Austin and R. H. H. Pierce, "The Linear Thermal Expansion and α-γ Transformation Temperature (A_3 Point) of Pure Iron," Transactions, American Society for Metals, Vol. 22, May 1934, p. 447.

Table I
Description of Irons

No. of Iron	Kind of Iron	Time and Temperature of Hydrogen Treatment	Chemical Analyses												
			Cu	Ni	S	Si	Sn	Mn	Cr	Mo	C	P	O_2	N_2	H_2
1	Carbonyl	250 hours 1200°C.	0.0033	0.0054	0.00013	0.002	.....	<0.004	<0.0005	0.002	0.0012	.....	.....	.....	.....
3[2]	Carbonyl	500 hours 1200°C.	0.0012	0.0068	0.00005	0.002	<0.001	<0.004	<0.0005	0.005	0.0018	0.005	0.002	0.003	0.0005
5	Carbonyl	500 hours 1450°C.	.....	.....	.....	.....	.....	.....	.....	.....	0.0023	.....	.....	.....	.....
7	Carbonyl	88 hours 1480°C.	.....	.....	.....	0.041	.....	.....	.....	.....	.....	.....	.....	.....	.....
8	Carbonyl	88 hours 1480°C.	.....	.....	.....	0.009	.....	.....	.....	.....	.....	.....	.....	.....	.....
10	Carbonyl	47 hours 1500°C.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
12	Armco	350 hours 1450°C.	.....	.....	0.005	0.005	.....	.....	.....	.....	.....	.....	.....	.....	.....
V53[1]	Electrolytic	None	.....	.....	.....	.....	.....	.....	.....	.....	0.012	.....	.....	.....	.....

Spectroscopic analyses made using irons 1, 3, and 5 showed traces of Cu, Ni, Si, Sn, Mn, Cr, and Mo are present.

[1]V53 is a vacuum-melted electrolytic iron.

[2]Since carbonyl iron from the same source was used to give irons 1, 3, and 5, it was not thought necessary to make a complete analysis of all three. Except for Si, irons 7, 8, and 10, which are also carbonyl irons, probably have a similar degree of purity as 3.

The apparatus is a mechanical-optical dilatometer, built of three composite Monel metal-quartz rods activating an optical lever which throws a beam of light on a revolving drum covered with photographic paper. Inserted in two of the rods are reference pieces of a 4 per cent silicon iron-silicon alloy (which possesses nearly the same coefficient of expansion as alpha iron and exhibits no transformation point) serving as reference standards; in the third rod is inserted the specimen under investigation. The reference standards and the specimen possess identical dimensions. The dilatometer unit is inserted in a quartz tube subsequently evacuated and heated externally by a furnace. The furnace is wound in sections so that thermal gradients may be eliminated (kept to less than ½ degree Cent.) by proper adjustment of the separate heating currents. A differential thermocouple is attached to the two ends of the specimen so that the temperature gradient may be read constantly. The specimen temperature was measured by means of a thermocouple inserted in the middle of the specimen; this thermocouple was connected to a temperature controller and through this determined the motion of the revolving photographic drum, thus automatically fixing the temperature scale registered there. In addition to the dilatometric curve a recording "Micromax" controller simultaneously furnished heating and cooling thermal curves. The rate of heating and cooling is constant and controlled by an electrical device to attain rates of ⅛, ½ and 2 degrees per minute. A comparison of curves A (Fig. 2), in which the temperature gradient in the specimen lengthwise was less than ½ degree Cent., with curves B, in which it was 10 degrees Cent., indicates that the gradient in the specimen must be kept as low as possible. It seems certain that the reported temperature differences between the beginning and the end of the alpha-gamma transformation as judged from dilatometric curves were caused by temperature gradients in the specimen at the time of transformation.

The dilatometer curves were so drawn that a change in length of one inch on the recorded curve represented an actual change in length in the specimen of 0.002 inch. The temperature scale recorded was 30 degrees Cent. per inch. The curves shown in the figures are all reduced, but the original scale may readily be inferred from the data shown on the figures.

Two spools of thermocouple wire, 28 B & S gage, one of chromel and the other of alumel, were used throughout the work.

Eight couples of this wire from different parts of the two spools were calibrated; the millivoltage readings for these various couples agreed within the accuracy of potentiometric readings, namely, ±0.05 degrees Cent. These calibrations were made against the melting and freezing points of pure aluminum, and also against a primary platinum, platinum-rhodium couple bearing a Bureau of Standards calibration certified as accurate to ± 0.5 degree Cent. over a temperature range of 0-1100 degrees Cent. (30-2010 degrees Fahr.).

Direct calibration against the melting and freezing points of aluminum was conducted in accordance with the recommendations of the Bureau of Standards.[10] A conversion table giving the millivolt-temperature relationship for chromel-alumel couples[11] was used in this calibration. Two entirely independent calibrations gave freezing points of 659.8 and 660.0 ± 0.1 degrees Cent. (1220 degrees Fahr.) (as read from the conversion table); the average of these values is only 0.2 degree Cent. above the accepted freezing point of the aluminum used, 659.7 ± 0.1 degrees Cent. The temperature of the aluminum remained constant within ± 0.1 degree Cent. for five minutes during freezing; the freezing and melting points were found to be identical.

The calibration by comparison with a primary platinum, platinum-rhodium couple showed the chromel alumel couple wire to read 0.5 degrees Cent. too high throughout the range 500-950 degrees Cent. (930-1740 degrees Fahr.). This correction was thenceforth applied to all temperature readings, and the accuracy of the primary couple, namely, 0.5 degree Cent., taken as valid also for the chromel-alumel couple. This may seem unjustified inasmuch as a secondary couple cannot justifiably bear the same limits in accuracy as the primary couple against which it was calibrated, but since the calibration of the chromel-alumel couple against the freezing point of aluminum showed a difference well within ± 0.5 degree Cent., it is felt that the assumed limits of ± 0.5 degree Cent. are really justified.

In accurate thermometric work it is not only necessary to procure proper calibration but also to secure evidence that this calibration is correct for the experimental conditions under which the temperature measuring device is used. Several experiments were performed on this point. In order to investigate the effect of heat flow along the wire adjacent to the hot junction (which differed in calibra-

[10]Technologic Paper 170, Bureau of Standards, 1921.

[11]Leeds and Northrup Conversion Tables, designated as "Std-1031, 21-11-30."

tion and in use), the hot junctions of two couples were placed close together and heated to 650 degrees Cent. (1200 degrees Fahr.) in such a way that the temperature remained nearly constant over a 2-inch length in one couple, while in the other a temperature gradient of more than 100 degrees Cent. obtained; the measured temperatures of the two junctions agreed to ± 0.05 degree Cent. Since in the experimental work the couple operated in a vacuum (which led a critic to call into question the applicability of the calibration), determinations were made on the Ac_3 and Ar_3 temperatures of a single specimen of pure iron, first in vacuum and then in argon; these temperatures were the same within 0.5 degrees Cent. In a further test on this point, a melting curve was taken of the primary aluminum standard held within the vacuum furnace, with all other arrangements the same as during a standard run; the observed melting point was 660.0 degrees Cent. (1220 degrees Fahr.), a temperature within 0.3 degree Cent. of the accepted melting point.

The method of attaching the thermocouple to the specimen is also of possible importance with respect to the accuracy of the thermometric work. In the usual practice, the thermocouple bead was inserted through a hole drilled in the center of the specimen, and then hammered into the soft specimen. Separate tests were made in which the bead was spot-welded to the specimen, in one case, and in which the bead was completely covered by flowing the soft metal of the specimen over it, in another; these tests gave temperature readings for the transformation points identical with those obtained using the practice first described.

Results Obtained

At heating rates of 2 degrees and ½ degrees Cent. per minute respectively, the Ac_3 thermal arrests were observed to be within 1 degree Cent. of one another, as were also the Ar_3 thermal arrests at similar rates of cooling. These arrests could not be observed with certainty at a rate of ⅛ degree Cent. per minute.

Reproducibility in dilatometric determinations of Ac_3 and Ar_3 depends greatly upon the magnitude of the temperature gradient in the specimen studied. With the proper control of temperature gradient (see above) it was found possible to secure an agreement within 1 degree Cent. for both Ac_3 and Ar_3, with less than 1 degree Cent. between the beginning and the completion of either trans-

formation, as shown in Fig. 1. The dilatometric curves shown in the figures are accurate tracings of the original photographic curves. The original curves could not be satisfactorily reproduced. When the temperature gradient was not controlled so precisely, consecutive dilatometric determinations of these points showed wider variations (Fig. 2), but with attention to proper control, results reproducible to ± 1 degree Cent. were obtained. It is apparent in Fig. 1 that the length changes in consecutive tests are not reproducible. This point will be discussed later.

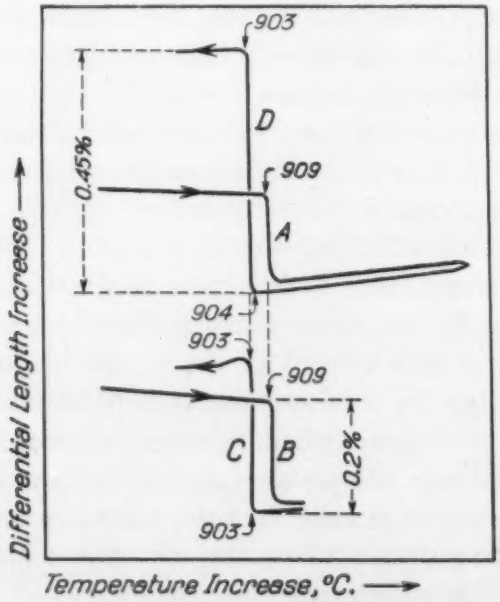

Fig. 1—Differential-Dilatation Temperature Curves. Rate of Heating and Cooling 2 Degrees Cent. Per Minute. Length Decrease at Ac_3 0.15 Per Cent (Curve A) and 0.18 Per Cent (Curve B). Length Increase at Ar_3 0.3 Per Cent (Curve C) and 0.45 Per Cent (Curve D). Length Scale, 1 Inch = 0.42 Per Cent. Temperature Scale, 1 Inch = 63 Degrees Cent. (As Printed; Reduction to 48 Per Cent of Original).

Fig. 3 shows that there is a close correlation between the thermal and the dilatation curves. It will be observed that curve C shows a spread of 4 degrees Cent. between the beginning and the end of Ac_3, whereas the thermal curve shows a sharp break midway in this range. This spread was identified as a result of a transverse temperature gradient (across the specimen rather than along it); a radiation shield partially eliminated this. When such a spread was encountered, the average value of the transformation temperature was taken. It must

be emphasized, however, that the dilatation curves used to evaluate the true A_3 temperature were those for which little spread in the transformation temperature was encountered. The close correlation between the thermal points and the dilatation points is evident in Tables III, V, VII and IX. Because of the uncertainty in the thermal points at rates of ½ and ⅛ degree Cent. per minute, only the dilatometric data are considered at these rates.

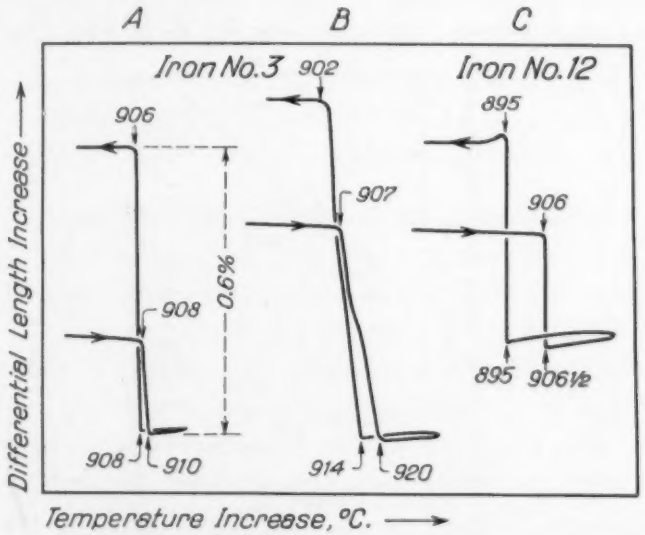

Fig. 2—Curves Showing Influence of Temperature Gradient in Specimen on Temperature Spread of Alpha-Gamma Transformation. Rates ½ Degree Cent. Per Minute (Curves A and B), and 2 Degrees Cent. Per Minute (Curve C). Temperature Gradient in Specimen Lengthwise ½ Degree Cent. in A and C and 10 Degrees Cent. in B. Length Scale, 1 Inch = 0.47 Per Cent. Temperature Scale, 1 Inch = 70 Degrees Cent. (As Printed; Reduction to 43 Per Cent of Original).

Discussion

Of the 57 determinations listed in the tables, only a few showed a difference of 4 degrees between the beginning and end of the transformation, and these were not considered in evaluating A_3. On heating, the difference amounted to 1 degree Cent. in 16 tests and ½ degree Cent. or less in 6 tests; on cooling, the difference amounted to 1 degree Cent. in 29 tests and ½ degree Cent. or less in 26 tests. As this suggests, the temperature difference between the beginning and the end of the Ac_3 transformation was observed to be consistently greater than between the beginning and the end of the Ar_3 transformation. It is possible that the greater tendency to undercool than to overheat may be responsible for this behavior, for undercooled specimens

once transforming might transform rapidly and at a nearly constant temperature, even though at an infinitely slow rate of cooling a real spread in temperature would be observed owing to the impurities present. In questionable cases, therefore, at faster rates, the temperature spread between the beginning and end of the transformation on cooling is only a doubtful indication of the purity. In relatively impure irons, such as hydrogen-purified Armco iron, the tendency to superheat is greater than in purer irons, and the argument may apply to a lesser degree here also; curves C in Fig. 2 show little or

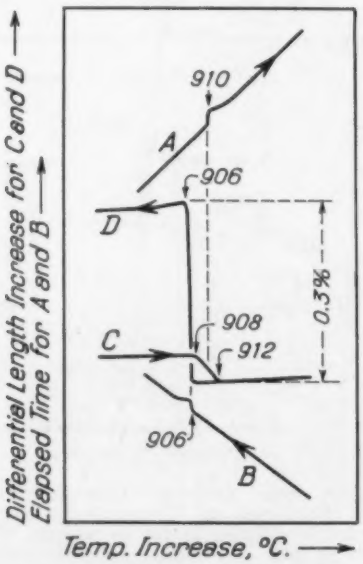

Fig. 3—Comparison Between Thermal and Dilatometric Curves. A and B—Heating and Cooling Time-Temp. Curves; Rate 2 Degrees Cent. Per Minute. C and D—Heating and Cooling Differential-Dilatation Temp. Curves; Rate 2 Degrees Cent. Per Minute. Length Scale (Dilatometric Curves C and D), 1 Inch = 0.38 Per Cent. Temperature Scale (Dilatometric Curves C and D, Thermal Curves A and B), 1 Inch = 57 Degrees Cent. Time Scale (Thermal Curves A and B), 1 Inch = 38 Minutes. (As Printed; Reduction to 53 Per Cent of Original).

no temperature spread at both Ar_3 and Ac_3 for this iron. The temperature spread for both Ar_3 and Ac_3 is somewhat greater for the purer iron. The argument given here is supported by the fact that no temperature spread was observed in relatively impure iron even when the longitudinal temperature gradient amounts to as much as 2 degrees Cent.

Table II

Alpha-Gamma Transformation Temperature Obtained in this Investigation

No. of Iron Used	Rates of Heating and Cooling in Degrees Cent. Per Minute: 2		½		⅛		
	Ac_3	Ar_3	Ac_3	Ar_3	Ac_3	Ar_3	A_3
1	909.5	904.5	910.0	906.5	909.0	907.0	909.5
3	909.0	904.5	910.0	906.5	909.0	907.0	909.5
5	909.5	904.5	909.5	905.0	909.5	907.0	909.5
7	910.5	906.0	911.5	909.0	910.5	908.0	910.5
8	909.5	906.0	.....	.....	910.5	907.0	910.0
10	.....	.....	.....	.....	909.0	906.0	909.0
12	906.5	893.5	906.0	896.5	904.5	897.0	902.0
V53	905.5	.....	905.5	900.5	.....	.....	905.5

Average data are listed for irons 1, 3, and 5 and individual data for 7, 8, 10, 12, and V53. 1, 3, 5, 7, 8, and 10 are hydrogen-treated carbonyl irons; V53 is a vacuum-melted electrolytic iron containing 0.012% C, and 12 is a hydrogen-treated Armco iron.

The alpha-gamma transformation temperatures determined in this investigation are listed in Table II, and may be taken as correct to within 1 degree Cent. In the case of the hydrogen-treated Armco iron (No. 12) the reported A_3 temperature may be in error by rather more than 1 degree Cent., because only a few tests were made using this iron, and the results obtained were not in agreement with those of the purer iron samples. It is also true that only a few data were obtained in the determination of the A_3 temperatures of irons 7, 8, and 10, but since these are high purity irons and the results agree with the average of all those obtained in tests using other high purity irons 1, 3, and 5, it is believed that the A_3 temperatures in irons 1, 3, 5, 7, 8, and 10 are accurate, as reported in Table II, to within 1 degree Cent.

As the most complete spectroscopic and chemical analyses were made of irons 1 and 3, most confidence may be expected in the results obtained using these irons (Table I). However, there is reason to believe that irons 5, 7, 8, and 10 have the same general order of purity as irons 1 and 3 with the exception that silicon is higher in 7 and may also be higher in 10. The constancy of the temperature arrest during the alpha-gamma transformation as indicated thermally, and the small temperature difference between the beginning and end of the transformation as indicated dilatometrically give general evidence that these irons do not contain appreciable amounts of soluble impurities which affect the A_3 transformation.

It will be observed in Table III to VIII that some of the data listed were obtained before all of the detectable sources of error were eliminated. For this reason the more recent results are held to

be the more accurate. Both old and new data are included since all of it are within 3 degrees Cent. of being correct, most of it within 2 degrees Cent. and the average within 1 degree Cent. The data referred to in the tables as good to 1 degree Cent. are the best obtained, and no data are included which indicate a spread at the alpha-gamma transformation of more than 1 degree Cent.

The data in Table II show that the Ac_3 temperature in high purity hydrogen-purified carbonyl iron is not appreciably affected by the rate of heating between 2 and 1/8 degrees Cent. per minute, so

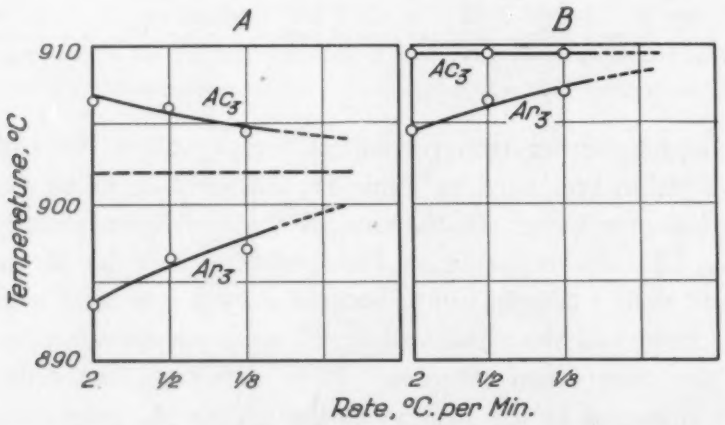

Fig. 4—Effect of Heating and Cooling Rate on the Temperature of Ac_3 and Ar_3 Transformations Using, A—Hydrogen-Purified Armco Iron and, B—Hydrogen-Purified Carbonyl Iron.

that it may be assumed that the A_3 transformation temperature is the same as the Ac_3 temperatures observed. For irons which showed a variation in the Ac_3 temperatures at different rates, the A_3 temperature was obtained by extrapolation as shown in Fig. 4a; these data were not used in evaluating the true A_3 temperature. It may also be noted from the results listed in this table that the A_3 temperature in all the hydrogen-purified carbonyl irons was found to be close to 909.5 degrees Cent. (1669 degrees Fahr.). The A_3 temperature on iron No. 3 was independently determined by Dr. J. B. Austin of the United States Steel Corporation Research Laboratory, using the dilatometer previously described (Ref. 9), yielding a value of 910 $\pm$ 1 degree Cent. This temperature is very close to those observed by Burgess and Crowe,[12] and of Benedicks[13] who used (presumably) high purity electrolytic irons in their investigations. In view of the consistency of the numerous results obtained in the pres-

[12]Ref. 1.
[13]Ref. 4.

Table III
Dilatometric and Thermal Analysis Data Using Iron No. 1

Rate of Heating and Cooling 2 Degrees Cent. Per Minute								
Dilatometric Ac_3 Data			Thermal	Dilatometric Ar_3 Data			Thermal	
Ac Begin. and End	Temp. Spread	Average	Ac_3 Data	Begin. and End	Temp. Spread	Average	Ar_3 Data	Remarks
908.5–910.5	2	909.5	.....	904.5–904.0	½	904.0	.....	[1]A
908.5–909.5	1	909.0	.....	904.5–902.5	2	903.5	.....	A
906.5–909.5	3	908.0	.....	.....	.	.....	.....	A
907.0–908.5	1.5	908.0	907.5	.....	.	.....	.....	[2]B
908.0–910.0	2	909.0	908.5	905.0	.	.....	.....	B
908.0	.	.....	908.0	903.0–902.5	½	903.0	902.5	B
912.0–913.0	1	912.5	913.0	907.5–907.5	0	907.5	907.5	[3]C
	Average	909.5	909.5			904.5	905.0	

[1]A—These tests were made before the temperature differential in the specimen was controlled as carefully as in subsequent tests and before the procedure of calibrating the temperature recorder against the type K_2 potentiometer before and after each test was used. These data are believed to be good to within about 2 degrees Cent.

[2]B—These data are rather better than those designated A. The temperature differential lengthwise in the specimen was kept below ½ degree Cent., but the temperature recorder was not checked before and after each test. These results are probably good to within 1½ degrees Cent.

[3]C—The temperature differential lengthwise in the specimen was kept below ½ degree Cent., and the temperature recorder was checked against the type K_2 potentiometer before and after each test. These data are believed good to within 1½ degrees Cent.

ent investigation, and the care taken with thermometry, the present authors believe they are justified in reporting the A_3 temperature in high purity iron as being 909.5 ± 1 degrees Cent. (1669 degrees Fahr.).

The presence of 0.042 per cent silicon in iron No. 7 may account for the slightly higher A_3 temperature noted, but the effect is small and the interpretation uncertain. The effect of the very small quantities of impurities present in the purest iron, as shown in Table I, seems negligible, judging from the known binary systems of these elements with iron; furthermore some of these elements tend to raise A_3 and others to lower it, the effects tending to cancel.

Table IV
Dilatometric Data Using Iron No. 1

Rates of Heating and Cooling in Degrees Cent. Per Minute								
½				⅛				
Ac_3 Begin. and End	Average	Ar_3 Begin. and End	Average	Ac_3 Begin. and End	Average	Ar_3 Begin. and End	Average	Remarks
907.5–910.5	909.0	906.5–903.5	905.0	907.5–909.0	908.5	908.0–906.5	907.5	[1]A
908.5–910.0	909.5	907.5–907.5	907.5	.....	.....	.....	.....	A
907.0–909.0	908.0	904.5–904.0	904.5	.....	.....	.....	.....	B
912.0–913.0	912.5	908.5–908.5	908.5	911.5–912.5	912.0	908.5–908.5	908.5	C
.....	.....	.....	.....	908.0–910.0	909.0	906.0–906.0	906.0	C
.....	.....	.....	.....	907.5–908.5	908.0	906.5–906.5	906.5	C
.....	.....	.....	.....	907.0–908.5	908.0	906.0–906.0	906.0	C
Average	910.0		906.5		909.0		907.0	

[1]For meaning of "A," "B" and "C" see Table III.

Average of 15 tests (Tables III and IV shows A_3 in iron No. 1 is 909.5 degrees Cent. (1669 degrees Fahr.).

Table V
Dilatometric and Thermal Data Using Iron No. 3

Rate of Heating and Cooling 2 Degrees Cent. Per Minute								
Dilatometric Ac_3 Data				Dilatometric Ar_3 Data				
Ac_3 Begin. and End	Temp. Spread	Average	Thermal Ac_3 Data	Ar_3 Begin. and End	Temp. Spread	Average	Thermal Ar_3 Data	Remarks
905.5–907.5	2	906.5[2]	905.5	902.5–902.5	0	902.5	902.5	A[1]
910.0–911.0	1	910.5	910.5	906.5–904.5	2	905.5	905.5	A
908.0–911.0	3	909.5	.....	904.5–904.0	½	904.0	904.5	B
905.5–909.5	4	907.5	.....	903.0–903.0	0	903.0	902.5	B
907.0–910.0	3	908.5	907.0	904.5–903.0	1½	903.5	903.0	B
906.5–911.0	4½	908.5	907.5	904.5	.	.....	903.5	B
906.5–910.5	4	908.5	907.5	905.0–904.0	1	904.5	903.5	B
908.5	.	.....	908.5	904.5	.	.....	903.5	B
908.0–912.0	4	910.0	910.0	907.5–905.5	2	906.5	906.5	C
.....	.	.....	.....	908.5–906.5	2	907.5	906.5	C
.....	.	.....	.....	905.5–905.5	0	905.5	905.5	
909.5–909.5	0	909.5	909.5	905.0–905.0	0	905.0	905.5	C
907.0–910.0	3	908.5	909.5	904.0–901.0	3	902.5	903.5	C
907.5–912.0	4½	909.5	909.5	903.0–901.5	1½	902.5	903.5	C
	Average	909.0	908.5			904.5	905.0	

[1]For meaning of "A," "B" and "C" see Table III.
[2]906.5 degrees Cent. (1665 degrees Fahr.) low because of instrumental error.

The data given in Table IX and represented in Fig. 5 for electrolytic iron containing 0.012 per cent show that this amount of carbon lowers the A_3 temperature by 4 degrees Cent. This may explain the somewhat lower results obtained on electrolytic iron by Esser[14] and by Sato.[15] Fig. 5 shows also the effect of carbon heterogeneity upon the range of the alpha-gamma transformation. Annealing for several hours above the A_3 temperature for the purpose of homogenization decreased this range from 35 to ½ degree Cent. (Table IX), showing that heterogeneity exerts a powerful effect upon such curves.

As stated before, the Ac_3 temperature is not affected by the rate of heating within the limits of temperature measurement attained, whereas the Ar_3 temperature is markedly affected. On the purest

Table VI
Dilatometric Data Using Iron No. 3

Rates of Heating and Cooling in Degrees Cent. Per Minute								
½				⅛				
Ac_3 Begin. and End	Average	Ar_3 Begin. and End	Average	Ac_3 Begin. and End	Average	Ar_3 Begin. and End	Average	Remarks
910.5–914.5	912.5	910.5–910.5	910.5	.....	.....	.....	.....	A[1]
911.5–912.5	912.0	909.5–907.5	908.5	.....	.....	.....	.....	A
907.5–909.5	908.5	907.5–905.5	906.5	.....	.....	.....	.....	B
907.5–908.5	908.0	905.5–905.5	905.5	.....	.....	.....	.....	C
.....	.....	905.5–905.5	905.5	908.0–909.5	909.0	907.0–906.5	907.0	C
Average	910.0		906.5		909.0		907.0	

[1]For interpretation of "A," "B" and "C" see Table III.

Average of 16 tests (Tables V and VI shows A_3 in iron No. 3 is 909.5 degrees Cent. (1669 Degrees Fahr.).

[14]Ref. 5.
[15]Ref. 6.

Table VII
Dilatometric and Thermal Analysis Data Using Iron No. 5

Rate of Heating and Cooling 2 Degrees Cent. Per Minute								
Dilatometric Ac_3 Data				Dilatometric Ar_3 Data				
Ac_3 Begin. and End	Temp. Spread	Average	Thermal Ac_3 Data	Ar_3 Begin. and End	Temp. Spread	Average	Thermal Ar_3 Data	Remarks
905.5–909.5	4	907.5	908.5	904.0–903.5	½	903.5	904.0	C[1]
906.5–910.5	4	908.5	908.5	904.0–903.5	½	903.5	903.5	C
910.5–911.5	1	911.0	912.5	906.5–905.5	1	906.0	906.5	C
910.0–910.5	½	910.0	.....	905.5–904.5	1	905.0	.....	D[2]
908.5–908.5	0	908.5	908.5	903.0–902.5	½	902.5	903.0	C
908.5–912.5	4	910.5	910.5	904.5–904.5	0	904.5	904.5	C
	Average	909.5	909.5			904.5	904.5	

[1]See Table III. (Data believed good to 1½ degrees Cent.).
[2]These data believed good to 1 degree Cent.

Table VIII
Dilatometric Data Using Iron No. 5

Rates of Heating and Cooling in Degrees Cent. Per Minute								
½				1/8				
Ac_3 Begin. and End	Average	Ar_3 Begin. and End	Average	Ac_3 Begin. and End	Average	Ar_3 Begin. and End	Average	Remarks
905.5–910.0	908.0	904.0–904.0	904.0	908.5–911.5	910.0	.....	.....	C[1]
.....	.....	.....	.....	908.5–912.5	910.5	909.5–909.5	909.5	C
.....	.....	.....	.....	906.5–909.0	908.0	906.0–902.5	904.5	C
910.5–911.0	910.5	906.0–906.0	906.0	909.0–910.0	909.5	907.5–907.0	907.5	D[2]
908.5–911.5	910.0	905.0–905.0	905.0	907.5–910.0	909.0	906.0–906.0	906.0	C
Average	909.5		905.0		909.5		907.0	

[1]See Table III. (Data believed good to 1½ degrees Cent.).
[2]These data believed good to 1 degree Cent. Average of 14 tests (Tables VII and VIII) shows A_3 in iron No. 5 is 909.5 degrees Cent.

Table IX
Dilatometric and Thermal Analysis Data Using Irons 7, 8, 10, 12 and V53
(See Table I)

No. of Iron	Heating and Cooling Rates °C./Min.	Dilatometric Ac_3 Data: Ac_3 Begin. and End	Dilatometric Ac_3 Data: Average	Thermal Ac_3 Data	Dilatometric Ar_3 Data: Ar_3 Begin. and End	Dilatometric Ar_3 Data: Average	Thermal Ar_3 Data
7	2	908.5–912.5	910.5	910.5	906.0–906.0	906.0	906.0
	½	909.5–913.5	911.5	.....	909.5–908.5	909.0	.....
	1/8	908.5–912.5	910.5	.....	909.0–907.0	908.0	.....
8	2	908.5–911.0	909.5	910.0	906.5–905.5	906.0	906.5
	1/8	909.5–911.5	910.5	.....	907.5–906.5	907.0	.....
10	2	908.0–909.0	908.5	.....	.....	.....	.....
	1/8	909.5–909.5	909.5	.....	.....	.....	.....
	1/8	908.0–909.0	908.5	.....	906.0–906.0	906.0	.....
12	2	906.5–906.5	906.5	907.0	894.0–893.0	893.5	894.0
	½	905.0–907.0	906.0	.....	897.0–896.0	896.5	.....
	1/8	904.0–904.5	904.5	.....	897.5–896.5	897.0	.....
V53	2[1]	877.0–912.0	.....	.....	893.0–874.0	.....	.....
	2[2]	904.0–907.0	905.5	905.5	898.0–895.0	896.5	.....
	½[2]	905.5–906.0	905.5	.....	900.5–900.5	900.5	.....

[1]This test was made when the 0.012 per cent carbon in V53 (vacuum-melted electrolytic iron) was very nonuniformly distributed in the iron.
[2]These tests were made after heating V53 to about 920 degrees Cent. (1688 degrees Fahr.) for approximately 20 hours, so that the carbon would be much more uniformly distributed in the iron in these than in the previous tests.

irons at the slowest rate used, ⅛ degree Cent. per minute, there is a difference of 2½ degrees Cent. between Ac_3 and Ar_3. Previous investigators have reported smaller differences for even faster rates, but these can hardly be real in view of the above discussion.

Decreasing the rate of heating from 2 to ⅛ degree Cent. per minute had little effect on the Ac_3 temperature in the electrolytic

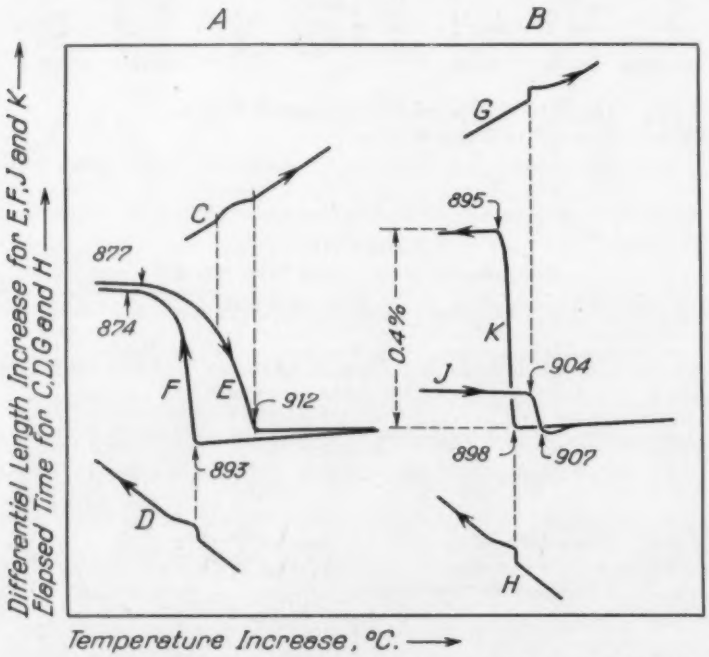

Fig. 5—Curves A Obtained Before and Curves B After the Carbon Was Uniformly Distributed in Iron V53 (0.012 Per Cent Carbon). Curves C, D, G, H Are Time-Temp. Heating and Cooling Curves. Curves E, F, J, K Are Differential-Dilatation Temp. Curves. Length Scale (Dilatometric Curves E, F, J, K), 1 Inch = 0.45 Per Cent. Temperature Scale (Dilatometric Curves E, F, J, K; Thermal Curves C, D, G, H), 1 Inch = 68 Degrees Cent. Time Scale (Thermal Curves C, D, G, H), 1 Inch = 45 Minutes. (As Printed; Reduction to 44 Per Cent of Original).

iron containing 0.012 per cent carbon. At a rate of ⅛ degree Cent. per minute the difference between Ac_3 and Ar_3 was 2 to 3 degrees Cent. This behavior is very similar to that observed for the high purity carbonyl iron containing possibly less than 0.001 per cent carbon. Apparently the most significant effect of a small quantity of carbon in iron is simply to lower the A_3 temperature.

A study of the behavior of hydrogen-purified Armco iron shows that the impurities (copper about 0.05 per cent) not only lower the A_3 temperature but modify the effect of heating and cooling rate on the temperatures of transformation, as may be seen from a com-

parison of curves A and B, Fig. 4. Both the Ac_3 and Ar_3 temperatures in the hydrogen-treated Armco iron were appreciably influenced by a change of heating and cooling rate from 2 to ⅛ degree Cent. per minute. The difference of temperature between the Ac_3 and Ar_3 transformations at the slower rate was 7½ degrees Cent., as compared with 2½ degrees Cent. under similar conditions using electrolytic or carbonyl irons.

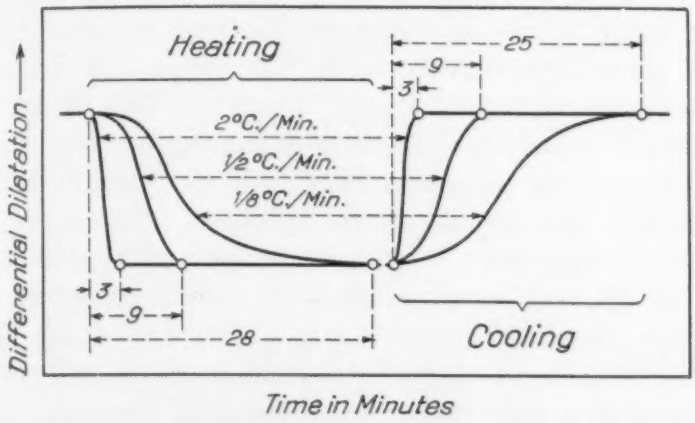

Fig. 6—Differential-Dilatation Time Curves of Iron No. 3 Showing the Influence of Rate of Heating and Cooling on the Time of the Reaction. Specimen Used Was 1 by ⅜ by ⅛ Inch.

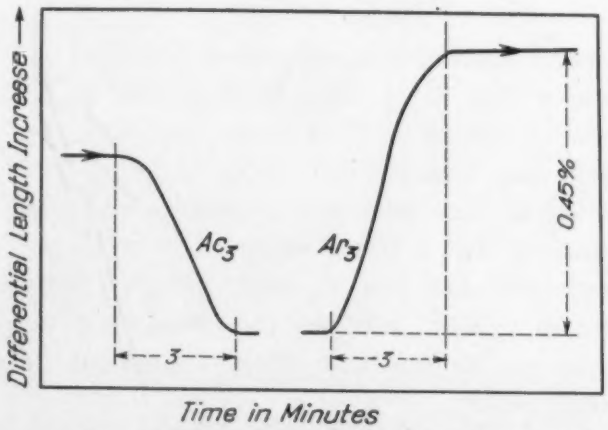

Fig. 7—Differential-Dilatation Time Curves of Iron No. 3. Rate of Heating and Cooling 2 Degrees Cent. Per Minute. Curves Designated Ac_3 Are Heating and Ar_3 Are Cooling Curves. Specimen Used Was 1 by ⅜ by ⅛ Inch. Length Scale, 1 Inch = 0.35 Per Cent. Time Scale, 1 Inch = 6 Minutes. (As Printed; Reduction to 48 Per Cent of Original).

By suitable adjustment of the dilatometer, time-dilatation curves (instead of temperature-dilatation curves) were taken for iron No. 3 at rates of heating and cooling of 2, ½, and ⅛ degrees Cent. per

minute, in order to show the influence of rate upon the time required for the alpha-gamma transformation. Curves such as those shown in Figs. 6 and 7 were obtained. It will be noted that surprisingly large amounts of time are consumed at the slower rates. These times must not be thought to contribute information on the times of the *constancy* of Ac_3 or Ar_3 temperatures. The constancy of these temperatures is shown on the temperature-dilatation curves. The times shown on these figures are simply the times required for the dilatometer to absorb (or to supply) the latent heat of transformation at the rates indicated. The rates of heating or cooling indicated are obviously nominal or furnace rates only and—at the transformation point itself—not the rate of the specimen. The curves in Fig. 7 (note that the time scale is much more open in this figure than in Fig. 6) show that the transformation on cooling begins much more abruptly than that on heating. Despite this fact equal times are consumed in the two reactions. Inasmuch as the transformation on cooling takes place only under an appreciable supercool potential, it may be inferred that at infinitesimal degrees of supercool or superheat the transformation on heating is much faster than that on cooling.

Typical temperature-dilatation curves obtained on high-purity iron are shown in Fig. 8. It may be seen that in three cases the samples contracted less on heating than they expanded on cooling. This observation has been made by several investigators.[16] Seigle ascribes this behavior to a preferred orientation of grains, but Austin and Pierce point out that it is not observed in less pure irons where preferred orientations can just as easily occur. Benedicks, whose specimens were in tension, ascribes the effect to a yielding of the material under stress, but the same effect is observed when the specimens are in compression.

To show that the effect is independent of any stresses introduced by the dilatometer, a carefully machined specimen of iron No. 3 was placed in the furnace on movable supports (not inserted in the dilatometer) and heated to above the transformation several times and then cooled to room temperature. This treatment produced an increase in length of 1.5 per cent.

The magnitude of the length changes observed may be read from Fig. 8. Judging from X-ray data on the density of alpha and gamma

[16] C. Benedicks, ref. 4; J. B. Austin and R. H. H. Pierce, ref. 9; M. J. Seigle, "Dilatometric Anomalies of Mild and Very Soft Carbon Steels," *Revue de Metallurgie*, Vol. 29, 1932, p. 169 and 252.

iron, the true length change should be 0.26 per cent of the specimen length. Fig. 8 shows that the observed changes were in the range 0.05 to 0.9 per cent. Occasional reverses in the effect were noted, as shown by curves C and D in Fig. 8. Slow rates of cooling invariably gave the effect shown in Curve D.

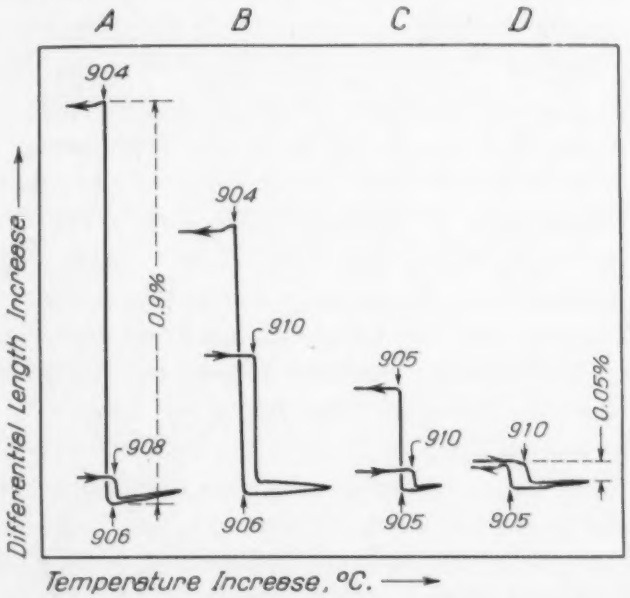

Fig. 8—Types of Differential-Dilatation Temperature Curves. Heating and Cooling Rate 2 Degrees Per Minute. A—Iron No. 1 Ac_3 Length Decrease, 0.05 Per Cent. Ar_3 Length Increase, 0.90 Per Cent. B—Iron No. 3 Ac_3 Length Decrease, 0.28 Per Cent. Ar_3 Length Increase, 0.60 Per Cent. C—Iron No. 5 Ac_3 Length Decrease, 0.04 Per Cent. Ar_3 Length Increase, 0.22 Per Cent. D—Iron No. 5 Ac_3 Length Decrease, 0.05 Per Cent. Ar_3 Length Increase, 0.05 Per Cent. Length Scale, 1 Inch = 0.50 Per Cent. Temperature Scale, 1 Inch = 75 Degrees Cent. (As Printed; Reduction to 40 Per Cent of Original).

At present there is no adequate explanation of this anomalous effect. The effect may be associated with the large grains used in this work; there is a rough correlation between purity and both the extent of the length changes and the difference in the length changes, but the evidence is not sufficiently clear. Dilatometric studies on single crystals will shortly be under way in this laboratory, and this may offer positive evidence.

Summary

About 60 dilatometric and thermal analyses of iron have been made using a new high-precision differential recording dilatometer.

Brief details on the construction and operation of this dilatometer are given; properly operated it has a sensitivity of less than 0.5 degree Cent. in the vicinity of 900 degrees Cent. (1650 degrees Fahr.). The iron used was prepared from selected Armco iron, and (especially) carbonyl iron by prolonged treatment in hydrogen at high temperatures, for periods varying between 47 hours and 500 hours, and temperatures varying between 1200 and 1500 degrees Cent. (2190-2730 degrees Fahr.). Vacuum-melted electrolytic iron was also studied. Chemical and spectroscopic analyses of carbonyl iron are given, showing it to be of unusually high purity. All thermometric work was done with thermocouples, and special attention paid to the functioning of thermocouples under experimental conditions. Heating and cooling curves were taken at rates of 2, ½, and ⅛ degrees per minute. The dilatometric results and thermal curves were in agreement, but only the dilatometric curves were useful at the slower rates. In the purest samples of iron the Ac_3 point was independent of the rate used, but the Ar_3 point showed a dependence upon rate; in iron samples of inferior purity the Ac_3 point showed a dependence upon rate. At the slowest rate the purest iron showed a difference of 2½ degrees Cent. between Ac_3 and Ar_3. An analysis of the data obtained fixed the A_3 point in pure iron at 909.5 ± 1 degrees Cent. (1669 degrees Fahr.). Heterogeneity in the distribution of as little as 0.012 per cent carbon in a sample of electrolytic iron spread the Ac_3 transformation over a range of 35 degrees Cent., which was reduced to ½ degree by annealing. In general the decrease in the length of the specimen on heating through Ac_3 was less than the increase in length on cooling through Ar_3, resulting in a net increase in the length of the specimen; the reason for this anomalous behavior is not known.

Acknowledgment

The authors wish to express their appreciation of the assistance rendered this work in the analyses of the iron used, in particular to Dr. R. M. Burns and Dr. R. M. Bozorth and the staff at the Bell Telephone Laboratories, to Dr. K. Burns of the Allegheny Observatory, and to Dr. J. G. Thompson of the Bureau of Standards.

DISCUSSION

Written Discussion: By F. T. Sisco, editor and metallurgist, Alloys of Iron Research, New York City.

The authors are to be congratulated, not only for the care and precision

used in their work, but also for choosing the determination of A_3 in high purity iron as a suitable project for research. There is no subject in ferrous metallurgy upon which more has been written, and about which less is known than the constitutional changes in high purity iron and iron-carbon alloys between room temperature and their melting point. No one who has not actually tried it, can realize what a headache results from trying to work out a ternary diagram of iron, carbon, and a third component when the transformations in iron-carbon alloys, and even the A_3 point in pure iron, are not known with reasonable accuracy. I am sure that all Alloys of Iron Research authors, at least, will join with me in hoping that the A_3 value of 909.5 degrees Cent. (1669 degrees Fahr.) given in this paper is the last word on the subject.

I am also gratified that this value, determined with so much accuracy on iron of such high purity, confirms the A_3 value of 910 degrees Cent. (1670 degrees Fahr.) recommended by Cleaves and Thompson of the National Bureau of Standards in our sixth monograph "The Metal—Iron." Cleaves and Thompson had to review and correlate more than 60 values with the best 18, determined on irons of exceptional purity, showing a spread of more than 30 degrees Cent. At the time the manuscript for this monograph was being reviewed a preliminary progress report by Dr. Mehl (February 1935) indicated that the Cleaves and Thompson value had received experimental verification. The publication of the authors' results gives us the final confirmation.

There is little in this paper which calls for comment. It is unfortunate that the authors dismissed the high A_3 values of 915 to 935 degrees Cent. (1679-1715 degrees Fahr.) obtained by Hensel and Larsen (Reference 9) on vacuum-fused and hydrogen-treated iron of high purity, with the brief statement that "recent investigators report that iron of this sort possesses an unusually high A_3 transformation (up to about 930 degrees Cent.)." We would like to see an explanation of this. Until it is forthcoming these high A_3 values will remain a slight but annoying thorn in our side.

The authors call attention to possible errors in Sato's 1928 data on A_3 (page 48). Recently we had occasion to check the data on iron-carbon alloys in this same paper and found that, in addition to the possible errors mentioned by the authors, the accuracy of Sato's method of extrapolation to zero rate is questionable. Sato used a straight-rate scale for extrapolation. If a semi-logarithmic or full logarithmic scale is used, Sato's A_3 will be considerably lower than his reported value of 903 degrees Cent. (1657 degrees Fahr.). No change in method of extrapolation by the authors would affect their A_3 point if Ac_3 is at a constant temperature as shown in Fig. 4B. If, however, Ac_3 changes with rate as in iron-carbon alloys, the method of extrapolation may affect the equilibrium A_3 temperature. It is to be hoped that the authors will make a study of this variable before reporting their final results on high purity iron-carbon alloys.

Written Discussion: By J. G. Thompson and H. A. Bright, metallurgist and chemist, respectively, National Bureau of Standards, Washington, D. C.

Messrs. Wells, Ackley, and Mehl are to be congratulated on their carefully conceived and painstakingly executed dilatometric studies. In connection with this paper a few remarks may be in order, regarding the purity of

carbonyl iron and the effect of prolonged treatment of high purity iron in hydrogen at high temperatures.

Carbonyl iron is accepted as being of high purity although most of the limited information available on this subject refers to spectrochemical data which are not as yet subject to quantitative interpretation. However, a recent publication from the National Physical Laboratory[1] contains an analysis of a carbonyl iron plate, from which it is concluded that "the purity of this material exceeds 99.9 per cent." Similar information is perhaps available in the files of other workers with high purity iron but analyses of sufficient accuracy and completeness to specify purities of over 99.9 per cent are practically nonexistent in the literature of iron. Accurate determination of the amounts of several impurities when the total of all impurities present is less than 0.1 per cent, is an analytical problem beyond the limits of the ordinary methods of ferrous analysis. Each determination is essentially a research investigation; the work must be done by a skilled analyst and at best the determinations are difficult and time consuming. It is not surprising that so few complete analyses of high purity irons have been reported.

The National Bureau of Standards is interested in pure metals and particularly in pure iron at the present time. Consequently analyses of two pairs of specimens were recently undertaken, each pair representing carbonyl iron before and after hydrogen treatment. One pair of specimens was prepared in Dr. Mehl's laboratory, the other by Dr. P. P. Cioffi of the Bell Telephone Laboratories. Arc spectra of the samples were examined for the sensitive lines of 49 metallic elements, and chemical analysis was employed for the quantitative interpretation of the spectrochemical data and for the identification of certain elements to which the spectroscope is not sensitive.

The results showed that both samples of untreated iron contained amounts between 0.001 and 0.005 per cent each of molybdenum, nickel, manganese, silicon, and carbon and also contained smaller amounts (probably less than 0.001 per cent each) of copper, tin, chromium, vanadium, and sulphur. Phosphorus could not be detected in 3-gram samples; if present at all the amount presumably is less than 0.0005 per cent. The presence of "faint traces" of magnesium and silver were indicated spectrochemically but these elements were not determined in the chemical analysis. The limits of accuracy of the analytical methods used are not well enough established to enable the expression in definite numerical figures of impurity contents of the order of 0.001 per cent each. It is highly probable, however, that the total of these determined impurities does not exceed 0.015 per cent for either of the specimens examined. Allowing for the probable presence of a few thousandths of a per cent each of oxygen, nitrogen, and perhaps hydrogen, the purity of these specimens prior to hydrogen treatment was definitely in excess of 99.9 per cent.

The most interesting indication from these analyses is in regard to the effect of the "hydrogen purification" on the composition of each of the irons. Spectrochemical results indicated that in each pair of specimens the contents of copper, manganese, tin and chromium were increased by the hydrogen treatment. Chemical analysis confirmed this indication and showed that the

[1]C. H. M. Jenkins and G. A. Mellor, "Investigation of the Behaviour of Metals Under Deformation at High Temperatures." *Journal*, Iron and Steel Institute, 1935. Preprint.

net result was to triple the total of the impurities content, increasing it from 0.015 to about 0.05 per cent. The principal increase was in the copper contents, from less than 0.001 to 0.013 and 0.025 per cent respectively in the two samples. Evidence of nonuniformity in the copper contents was encountered but the figures given represent the average content of each of the two specimens. Increases in manganese and tin were definite but less noticeable than for copper. A net decrease in purity, as a result of hydrogen treatment, was indicated in a qualitative manner by the rate of solution of the samples in dilute sulphuric acid; the hydrogen-treated material dissolved at a definitely faster rate than did the untreated samples.

These results indicate that the term "hydrogen purification" incorrectly describes the treatment which increased the impurity content of both of the specimens examined. It is true that this conclusion is based on examination of only two specimens but the evidence in both cases is unmistakable. Possible sources of this increase in metallic impurities during a treatment which has been assumed to be without effect on metallic constituents, may perhaps be suggested by those who are familiar with the details of construction and operation of the hydrogen treatment furnaces. The analyses indicate that the copper and manganese contents of Armco iron are approached in the hydrogen-treated carbonyl irons.

It is hoped that other investigators will undertake similar analyses, difficult and time consuming as they are, in order that the purity of carbonyl irons and the effect of hydrogen treatment at high temperatures may be definitely established.

Written Discussion: By L. L. Wyman, Research Laboratory, General Electric Co., Schenectady, N. Y.

The authors are to be congratulated, both for the development of the precision dilatometer used in this work, and for the excellent presentation of results obtained from this instrument.

I have had the privilege of seeing this machine in operation, and feel every confidence in the accuracies stated by the authors.

There is one source of error, however, which is seldom, if ever, taken into consideration in dilatometric work where the results are registered photographically on paper, and this error is due to the dimensional changes in the paper during its processing.

Dr. Mehl and his associates have developed a unique method of registering the calibrating temperatures directly on the paper, thus nearly eliminating this difficulty.

In dilatometers of the Chevenard type, utilizing a triangular tilt-table, the possible errors due to distorting the paper may amount to 4 to 5 per cent, as has been found by accurate checking.

The use of photographic films or plates will, of course, come as near as possible to eliminating this error and are to be recommended.

Written Discussion: By J. B. Austin, Research Laboratory, U. S. Steel Corporation, Kearny, N. J.

Several years ago, Mr. Pierce and I investigated the alpha-gamma transformation temperature of a number of samples of iron and concluded that in the pure metal this temperature must be close to 928 degrees Cent. (1700 de-

grees Fahr.). It was also observed that several samples of apparently comparable purity had quite different transformation temperatures. When Messrs. Wells, Ackley and Mehl kindly informed us that preliminary measurements in their investigation gave 910 degrees Cent. (1670 degrees Fahr) for the A_3 point it became clear that some considerable error was present in either their work or ours, and that the observed differences were due to one or more of three causes:

(1) A difference in the purity of the iron.
(2) An incorrect measurement of temperature.
(3) A difference in temperature scales.

An examination of exchanged samples quickly proved that a difference in the samples was not responsible, and that the error lay in the temperature.

Wells, Ackley and Mehl, making further checks on their method confirmed their temperature measurements and established them beyond question, as can be seen from their account in this paper. Meanwhile, Mr. Pierce and I, re-examining the refraction thermometer method which we had used, found an error arising from radiation at high temperatures combined with the insulation provided by the high vacuum. This error, which became increasingly greater above 700 degrees Cent. (1292 degrees Fahr.), not only accounted for a large part of the difference between two sets of observations but also explained most of the difference between samples of similar purity which we had found in our earlier work. A careful rechecking of the refraction thermometer scale disclosed a small error at these same temperatures which, when corrected for, brought our values into agreement with those reported in this paper. A report of our work is now being prepared for publication but we wish to state here that our results are now in entire agreement with those of Wells, Ackley and Mehl in placing the transformation temperature at 910 degrees Cent. (1670 degrees Fahr.).

Written Discussion: By Dr. Frank Adcock, received from Cecil H. Desch, The National Physical Laboratory, Teddington, Middlesex, England.

The authors' paper is of great interest to us especially as a short study of the dilatometric changes associated with the A_3 transformation in iron has been made by workers in this laboratory.[2] The specimens used by us were small cylinders measuring 7 millimeters in diameter by 15 millimeters in height (approximately) and under the conditions of the experiment it is unlikely that the temperature difference between the ends of any specimen could exceed 2 or 3 degrees Cent. Precautions were adopted to insure that the temperature of the specimen was accurately recorded by a thermocouple and risk of contamination was reduced to a minimum by employing an atmosphere of purified argon. The purest sample of iron available for the dilatometric tests gave on analysis for 31 elements, total impurities 0.0113 per cent plus traces, the most serious impurity being 0.0045 per cent carbon.

The dilatometric changes connected with the Ac_3 and Ar_3 in this material were found to be spread over temperature intervals of 26 and 12 degrees Cent. respectively. As mentioned above, it is not considered that a serious temperature gradient could exist in the specimen, and this view is supported

[2]F. Adcock and C. A. Bristow, "Iron of High Purity." Paper recently accepted for publication by The Royal Society, Great Britain.

by the sharply defined beginning and end of both the Ac_3 and Ar_3 range. These temperature ranges are much greater than those found by the authors. Further, the average value for the A_3 change in the high purity iron sample mentioned above, was 924 degrees Cent. (1695 degrees Fahr.)—a value considerably higher than the authors' mean value. It is difficult to assign a reason for these discrepancies, other than that the A_3 change may be complex and that unknown factors may be in operation. The transformation may be influenced in our case by the argon atmosphere employed, and it is hoped to repeat some of our experiments shortly in vacuo. Experiments with high purity irons containing up to 0.0035 per cent nickel and 0.0039 per cent phosphorus also gave definite temperature ranges but the influence of these impurities on the actual location of the ranges could not be correlated.

We look forward with pleasurable anticipation to the results of the proposed experiments with single crystals and hope that these will throw more light on the anomalous dimensional change already mentioned.

Oral Discussion

T. D. YENSEN:[3] When, a few years ago, I suggested that pure iron may have no allotropic transformations, it was done with the hope that such an unorthodox idea would stimulate investigators to a rigorous attack on the problem of determining whether or not this might be so and if so, what the transformation is due to. During the past few years a number of investigations have tended to show that the A_3 point is increased with increasing purity. I think the authors have pointed this out in the paper. The present authors have done a very nice piece of work. They have taken every precaution to eliminate errors in measurements, and as to the purity of the samples, they are probably purer than samples used by previous investigators. One would therefore, be inclined to concede the point that pure iron actually goes through allotropic transformations, and that the A_3 point is close to 910 degrees Cent.; the same value as given a number of years ago.

There is only one point on which I should like to raise a question. The samples were all hydrogen-annealed at a high temperature before being tested for transformation, after which they were analyzed for impurities. While no carbon analysis is given is seems probable in view of our experience that the carbon content of the samples is very low, say, 0.001 to 0.003 per cent.

Now, the samples were placed in a quartz tube externally heated and subsequently evacuated. In other words, the transformation points were measured in a vacuum. While this may seem like a safe procedure we should not take it for granted, and I wish to give some evidence that it is not a safe procedure. Samples of iron annealed in hydrogen at high temperatures have been found to have a maximum magnetic permeability of over 200,000, and this high permeability has been conceded to be due to high purity. When such a sample is subsequently annealed in a good vacuum at 900 degrees Cent., the maximum permeability is found to drop considerably, perhaps to one tenth of its former value. At first, it was suggested that this drop is caused by removal of hydrogen, but subsequent tests have eliminated this idea. I suggested in 1932 that it was due to oxidation, and I am still inclined to this belief. We have

[3]Westinghouse Electric and Manufacturing Co., E. Pittsburgh, Pa.

no absolute proof, but one thing is sure, something happened to the iron during the vacuum annealing. It reminds me of the story of Ole, who was walking with his friend along the railroad track. When a train came along Ole disappeared from view. His friend continued walking along the track. After a while he picked up a leg, then an arm, and finally, a head. Based on this evidence he drew this profound conclusion: "Something has happened to Ole." What apparently happened to Ole, is not more profound than what happened to the pure iron in vacuum annealing, and it would be highly desirable to have this question cleared up before accepting the verdict as final that pure iron has allotropic transformation.

F. M. WALTERS:[4] In view of the fact that I designed the dilatometer used in this investigation, I am going to take the liberty of answering the criticism in regard to the use of photographic paper in recording the transformation points. When I was using this piece of apparatus it was my procedure to put the identifying temperature marks on the paper, either two of them to cover the range of the transformation, or a single mark at such a position that the error in measuring between the transformation and the indicated temperature would be very small.

Authors' Closure

BY C. WELLS

The authors wish to thank Mr. Wyman for his comments and for pointing out that an important precaution so often neglected in previous dilatometric investigations was taken in the present one. Providing one corrects for paper dimensional changes, as was done by the authors, there is no necessity to use films, although in some cases it may be more convenient to do so.

It is very pleasant to receive Dr. Austin's discussion and to find that both his and the authors' results are now in perfect agreement.

The comments of Mr. Sisco are very welcome. It is gratifying, as Mr. Sisco points out, that the A_3 figure appearing in the monograph "The Metal—Iron"[5] and recommended by Cleaves and Thompson, agrees with that given by the authors. However, the method of averaging A_3 data showing considerable spread, as was done by Cleaves and Thompson, is not very satisfactory, and it is believed that the excellent agreement between the average A_3 temperature given by them and that of the present authors is accidental. Apparently Mr. Sisco thinks that an explanation of the high A_3 reported by Hensel and Larsen[6] should be offered. The data reported in the investigation of their purest iron show the Ac_3 transformation to be about 920 degrees Cent. (1688 degrees Fahr.). The rate of heating was 20 to 25 degrees Cent. per minute which, according to Burgess and Crowe,[7] is sufficient to raise the A_3 in iron by about 10 degrees Cent. From this it seems that the A_3 in the best iron used by Hensel and Larsen should have been reported as being about 910 degrees Cent. (1670 degrees Fahr.). This figure would have agreed with that given by the present authors.

Since the Ac_3 and A_2 temperatures in high purity iron are practically

[4]Research Engineer, The Youngstown Sheet & Tube Co., Youngstown, O.
[5]H. E. Cleaves and J. G. Thompson, "The Metal—Iron," Reinhold Publishing Corp.
[6]Ref. 9.
[7]Ref. 1.

identical at rates of heating of less than 2 degrees Cent. per minute, the question of extrapolation to "zero rate" mentioned by Mr. Sisco does not arise in the determination of A_3 in high purity iron. The Ac and Ar data on the least pure iron (Armco) used in the present investigation were plotted semi-logarithmically, and then extrapolated to "zero rate" (Fig. 4A). This is the most convenient method of extrapolation, and is also applicable to the data obtained when using iron-carbon, hypoeutectoid alloys. No matter which of the various methods of extrapolation[8] to "zero rate" are applied to these data the final results agree to within 1 degree Cent.

The authors wish to thank Drs. Thompson and Bright for their discussion. They refer to the increase in copper, manganese, tin, and chromium in certain hydrogen-treated irons, and question the use of the term "hydrogen purification" to describe a treatment which they claim increased the impurity content of the hydrogen-treated carbonyl iron specimens they examined. It is quite obvious that these increases in impurity after high temperature hydrogen treatments can only have come from the surroundings during those treatments. In the present investigation precautions were taken to limit impurities in the surroundings as much as possible. Hydrogen-treated carbonyl iron supports were used, and these rested on chemically pure magnesia which separated the carbonyl iron charge from the Armco tube and thereby limited the diffusion of impurities from the tube to the iron being purified. The chemical analysis made after the purification on irons 1 and 3 (Table I) shows that any increase of impurity while these irons were being purified must have been quite small, certainly very much smaller than one might conclude from the remarks of the discussors. It should be emphasized here that the irons referred to by the discussors were hydrogen-treated under different conditions from those prevailing when the irons used in this investigation were hydrogen purified, so that their results and the authors' results are not strictly comparable.

The objection to the term "hydrogen purification" appears to be unjustified in view of the fact that oxygen, completely removed during the hydrogen treatment, is generally of the order of 0.2 per cent in carbonyl iron as received. This amount is far greater than the total increase of impurities reported by Drs. Thompson and Bright.

It is very pleasant indeed to have Dr. Yensen, who, with Mr. Ziegler, has spent considerable time in the preparation and study of high purity irons, express his opinion that the irons used in the present investigation are probably purer than those used by previous investigators. It is also interesting to find that Dr. Yensen, who first suggested that pure iron may have no allotropic transformation, now feels inclined to concede the point that pure iron actually goes through an A_3 allotropic transformation at about 910 degrees Cent. (1670 degrees Fahr.).

During the investigation every effort was made to secure as complete and as numerous analyses as possible on the irons used. When the paper was preprinted no carbon analyses were available, but are now added to Table I.

The doubt expressed by Dr. Yensen arising from the fact that tests were

[8]Rates of heating and cooling were plotted both linearly and logarithmically against the temperature of transformation. The cube roots and fourth power roots of the rates of heating and cooling were also plotted against this temperature. In all cases the curves obtained were then extrapolated to "zero rate."

made in vacuum should be dispelled, since in three consecutive tests using a 2 degrees Cent. per minute rate of heating, one made using a vacuum, another an atmosphere of argon, and a third an atmosphere of hydrogen, the observed Ac_3 temperature was 910 ± 1 degree Cent.

The authors are pleased to have the discussion by Dr. Desch. Adcock and Bristow's results referred to by Dr. Desch not only are in disagreement with those obtained in the present investigation, but are inconsistent with the commonly accepted viewpoint that a phase transformation in a pure metal should take place at one and only one temperature under equilibrium conditions.

It has already been shown that a pronounced carbon heterogeneity (Fig. 5a) and a high temperature gradient (Fig. 2b) in a specimen during a transformation increase the Ac_3 and Ar_3 temperature ranges considerably. No information has been received to show that the carbon in Adcock and Bristow's iron was uniformly distributed. The small amount present, 0.0045 per cent, may be responsible for several degrees spread observed between the beginning and end of the A_3 transformation. With reference to temperature gradients during the transformations in the specimens used by Adcock and Bristow, it must be said that without knowledge of the actual gradients from direct measurement there is no conclusion as to the extent of the gradient; in addition, no information regarding the position of the thermocouple hot junction relative to the hottest or coldest spot in the specimen has been given. If one were to assume that the 26 degrees Cent. temperature range at Ac_3 mentioned by the discussor was caused by a temperature gradient and that the thermocouple was located at the hottest spot in the specimen during the transformation, the corrected A_3 temperature would be 911 degrees Cent., i.e., in agreement with author's results. Of course, if, as Dr. Desch believes, the specimen temperature gradient referred to must be less than 2 or 3 degrees Cent., then the above explanation is only partially satisfactory. The discussor states that the sharply defined beginning and end of the Ac_3 and Ar_3 transformation temperature range supports his belief, but a reference to Fig. 2b clearly indicates that a temperature gradient of 15 degrees Cent. or more may exist in a specimen and the beginning and end of the Ar_3 range may still remain sharply defined on the dilatometric curves. At any rate a more critical study of Adcock and Bristow's results will have to remain until those results are published and more is known about the rates of heating and cooling used, precautions taken to insure a uniform distribution of carbon and low specimen temperature gradients, and whether or not the calibrations of thermocouples were made using the same conditions as in the tests.

Comparison of the purity of the iron used by the authors and by Adcock and Bristow indicates that all the irons used had about the same purity.

It has been pointed out above that the A_3 in high purity iron is not affected by argon so that it is not expected that any appreciable difference will be observed between the results now submitted by Dr. Desch and those to be obtained in his laboratory using a vacuum. During tests in which argon and several hours of heating were used the chromel-alumel thermocouples deteriorated resulting in erroneously low temperature observations. For this reason such observations were discarded except where tests were sufficiently short to avoid appreciable deterioration of the thermocouple.

AUSTENITIC GRAIN-SIZE IN CAST IRON

By D. W. Murphy and W. P. Wood

Abstract

Evidence is presented which shows that the properties of gray cast iron are powerfully affected by variations in the austenitic grain-size of the material. Increasing austenitic grain-size increases the as-cast strength and hardness. The hardenability of gray cast iron is shown to increase with increasing austenitic grain-size and that the effects of grain-size on strength and hardness may possibly be due to the effect of grain-size on hardenability. It is pointed out that further study of this variable from the standpoint of control as well as its effects on properties should prove enlightening. The importance of the question of hardenability in gray cast iron, particularly with the greater application of heat treating, is discussed.

THE frequent erratic behavior of the properties of gray irons of apparently the same composition even when conditions are the same has concerned many metallurgists and users of cast iron. Some attribute these variations to hereditary characteristics derived from the pig iron charged, while others believe that the type of coke has a great influence on the type of metal produced from a cupola furnace. Both theses are quite possibly justifiable and yet the precise differences in structural characteristics which are associated with the variation of properties have not been identified.

Up to the present time, two structural characteristics of gray iron have been recognized as affecting the physical properties of the iron. One of these is the amount, size and distribution of the graphite flakes. These flakes in a sense are inclusions which may destroy the continuity of the matrix. The cooling rate, which is a function of the size of the section, pouring temperature, the type of mold, the chemical composition (especially the relation of silicon to carbon and the presence or absence of alloying elements), and the

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melting practice are the chief contributors to the variations of the graphite phase in gray cast iron. The other structural factor whose influence on properties is widely recognized is, of course, the condition of the matrix, namely, whether it is ferritic, pearlitic, sorbitic, troostitic, martensitic or austenitic just as in steel. Naturally since the matrix of cast iron is exactly like the matrix of steel, it will be affected by the same variables in the same manner as is steel.

The work of Bolton, Bornstein, MacPherran, MacKenzie and others has amply demonstrated the importance of strict and unrelenting control of raw materials and processes which is necessary to secure a reasonable degree of consistency in the properties of gray iron. The work of identifying and controlling the various factors which influence the structural composition and the resulting physical properties of gray cast iron has in no small measure contributed to the somewhat startling advances in the uses and in the quality of the product of the gray iron foundry. One has only to glance through the recent symposium on cast iron held by the American Foundrymen's Association and the American Society for Testing Materials in June 1933 to be impressed with the rapid strides of the foundry industry in recent years. As the knowledge of the control of cast iron broadens, the requirements which the material must meet increase. But in spite of the advances of recent years it is not uncommon to find wide fluctuations in the properties of gray cast irons of similar analyses and structure. So much is this true, that today there is a decided tendency to regard chemical composition specifications as of secondary importance.

The question naturally arises, therefore, as to what is responsible for this apparently anomalous behavior. It is the intent of this paper to show that one possible explanation may be found in the variation of the austenitic grain-size in the iron. It should be pointed out here that the austenitic grain-size which will be discussed is not the grain-size ordinarily considered in dealing with gray iron. Most foundrymen at present interpret grain-size on the basis of fracture appearance which is closely connected with graphite flake size and distribution. From this standpoint close, or fine-grained irons are ordinarily found to be strongest.

Without attempting a detailed exposition of the effects of grain-size variation on the properties of steel, it will be worth while to recall some of the principal characteristics of its influence in the case of steel.

It has been shown by Davenport and Bain[1, 2] and by Grossmann[3] that the ability of a steel to harden by quenching is dependent to a great extent on the inherent grain-size tendencies of that steel; steels having an inherent tendency toward large grains are deep hardening while those having a tendency toward fine grains are shallow hardening. Further it has been observed that steels of the coarse-grained types will frequently show higher strength properties than those of the fine-grained type, particularly in the normalized condition. Likewise differences in hardness between coarse and fine-grained steels frequently occur, the former type showing the higher hardness values. The impact resistance and ductility of the fine-grained steels are normally higher than those of the coarse-grained steels. In the heat treating operation, fine-grained steels show a lesser tendency toward distortion on quenching than do the coarser grained steels. The importance of grain-size in steel is apparent when it is considered that the large consumers almost uniformly buy steel on specifications containing very definite grain-size requirements.

In order to determine whether or not an austenitic grain-size variation in gray cast iron was at least partly responsible for variations in properties it was first necessary to develop a means by which such grain-size variation could be observed. A series of tests were made on two cast irons poured on the same day from a cupola operating continuously and under close supervision. The tests consisted of heating samples about 1 inch long with a cross section of $\frac{9}{32}$ by $\frac{5}{32}$ inch to various temperatures ranging from 1290 to 1830 degrees Fahr. (700 to 1000 degrees Cent.) for 30 minutes, cooling in dry sand, polishing and etching, and then examining them at low magnification. It soon developed that the network was readily stained by nitric acid and picric acid reagents until it was nearly the same color as the matrix. The method finally adopted was to etch for a short time in 4 per cent nital followed by immersion for 2 minutes in an aqueous solution of chromic acid (10 per cent). The specimen was

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[1]E. S. Davenport and E. C. Bain, "General Relations Between Grain-Size and Hardenability and the Normality of Steels," TRANSACTIONS, American Society for Metals, Vol. 22, No. 10, 1934, p. 879.

E. C. Bain, "On the Rates of Reactions in Solid Steel," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 100, p. 13.

[2]E. C. Bain, "Factors Affecting the Inherent Hardenability of Steel," TRANSACTIONS, American Society for Metals, Vol. 20, No. 5, p. 385.

[3]M. A. Grossmann, "Grain-Size in Metals with Special Reference to Grain Growth in Austenite," TRANSACTIONS, American Society for Metals, Vol. 22, No. 10, 1934, p. 861.

M. A. Grossmann, "On Grain-Size and Grain Growth," TRANSACTIONS, American Society for Metals, Vol. 21, No. 12, 1933, p. 1079.

Table I
Chemical Composition and Ultimate Strength

Iron No.	Total Carbon	Graphitic Carbon	Carbon Combined	Manganese	Silicon	Ultimate Strength Lb./Sq.In.
1	3.75	3.05	0.68	0.55	2.86	40,300
4	3.73	3.13	0.60	0.54	2.88	53,100
8	3.73	3.11	0.62	0.57	2.93	37,400
6	....	....	....	....	....	41,000
4A	2.57	1.91	0.66	0.51	1.98	.....
4B	2.41	1.71	0.70	0.52	1.98	.....

then retouched on the last polishing wheel to remove the stain, and if necessary the etching with chromic acid and retouching on the wheel was repeated until satisfactory resolution was obtained. For the particular type of iron studied, it was found as a result of these tests that the network was most easily developed in the samples treated at 1560 and 1650 degrees Fahr. (850 and 900 degrees Cent.). Accordingly, the grain-size determinations were made on samples heated in this range since this series of tests also showed that for the short exposure of 30 minutes no difference in grain-size was developed between the upper and lower temperature limits.

The next step was the selection of a series of irons of the same cross section whose ultimate strengths had been determined and subjecting them to the procedure outlined in the preceding paragraph. The chemical compositions and ultimate strengths of these irons are recorded in Table I. However only one of the irons of intermediate strength was analyzed. Figs. 1a to 4a show the grain-size characteristics of these irons as observed after the heat treatment, while Figs. 1b to 4b show the graphite distribution in the same irons. Figs. 2b, 3b and 4b show a practically constant type of graphite distribution, while Fig. 1b shows a somewhat different distribution. The chemical analyses show little if any difference, yet the ultimate strengths vary from 37,400 pounds per square inch for Iron No. 8 to 53,100 pounds per square inch for Iron No. 4.

It is apparent on examining Figs. 1a to 4a that while neither the chemical analyses nor the graphite characteristics of the four irons are markedly different, the grain-size characteristics are vastly different. Iron No. 8 is characterized by fine grain, Iron Nos. 1 and 6 by intermediate grain and Iron No. 4, the strongest iron by a very coarse grain. In other words as the grain-size increases the strength increases, provided other factors remain constant. It should be emphasized that this finding is directly opposed to the customary inter-

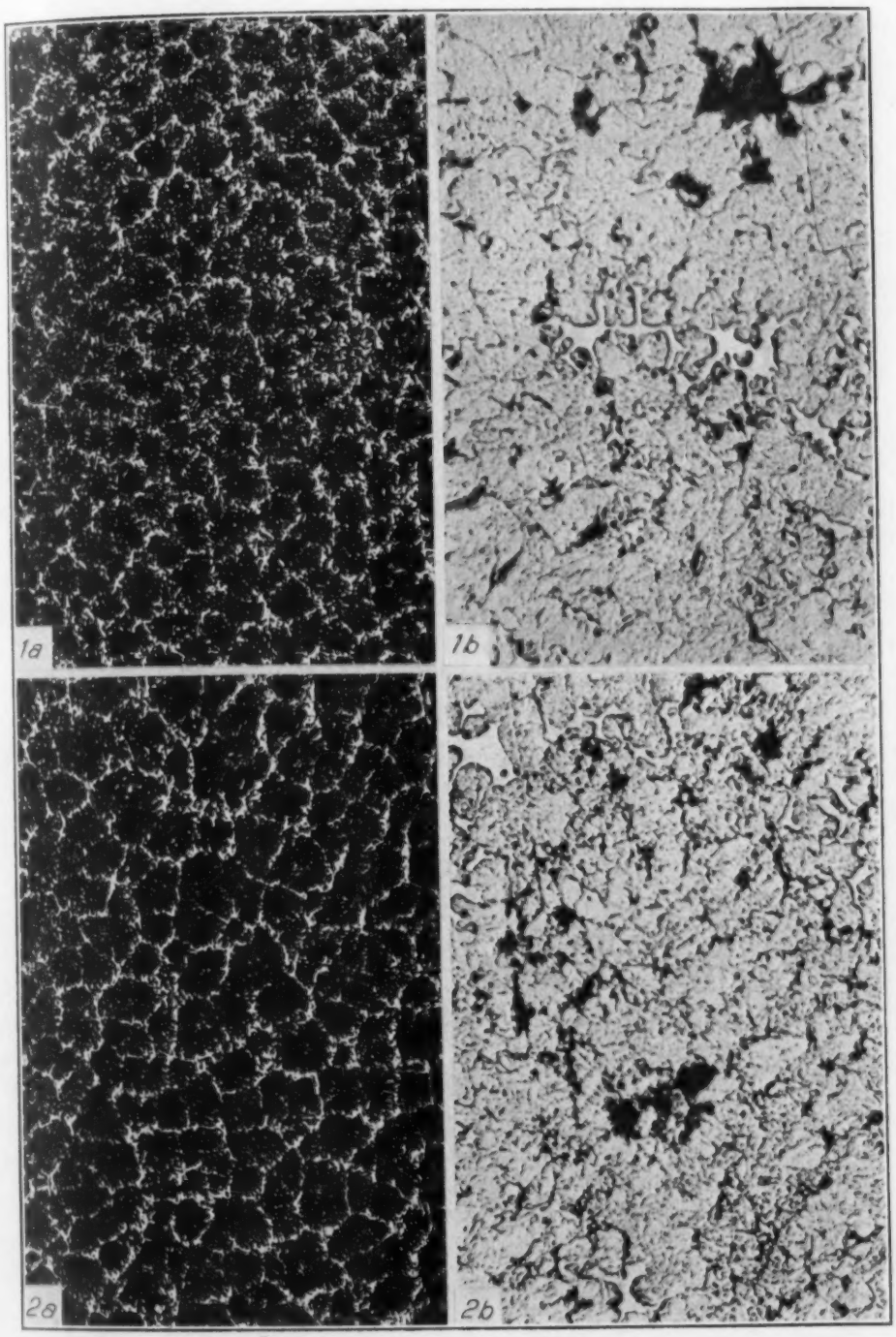


Fig. 1a—Grain-Size of Iron No. 8. Tensile Strength 37,400 Pounds Per Square Inch. × 40. Fig. 1b—Graphite Distribution of Iron No. 8. × 300. Fig. 2a—Grain-Size of Iron No. 1. Tensile Strength 40,300 Pounds Per Square Inch. × 40. Fig. 2b—Graphite Distribution of Iron No. 1. × 300.

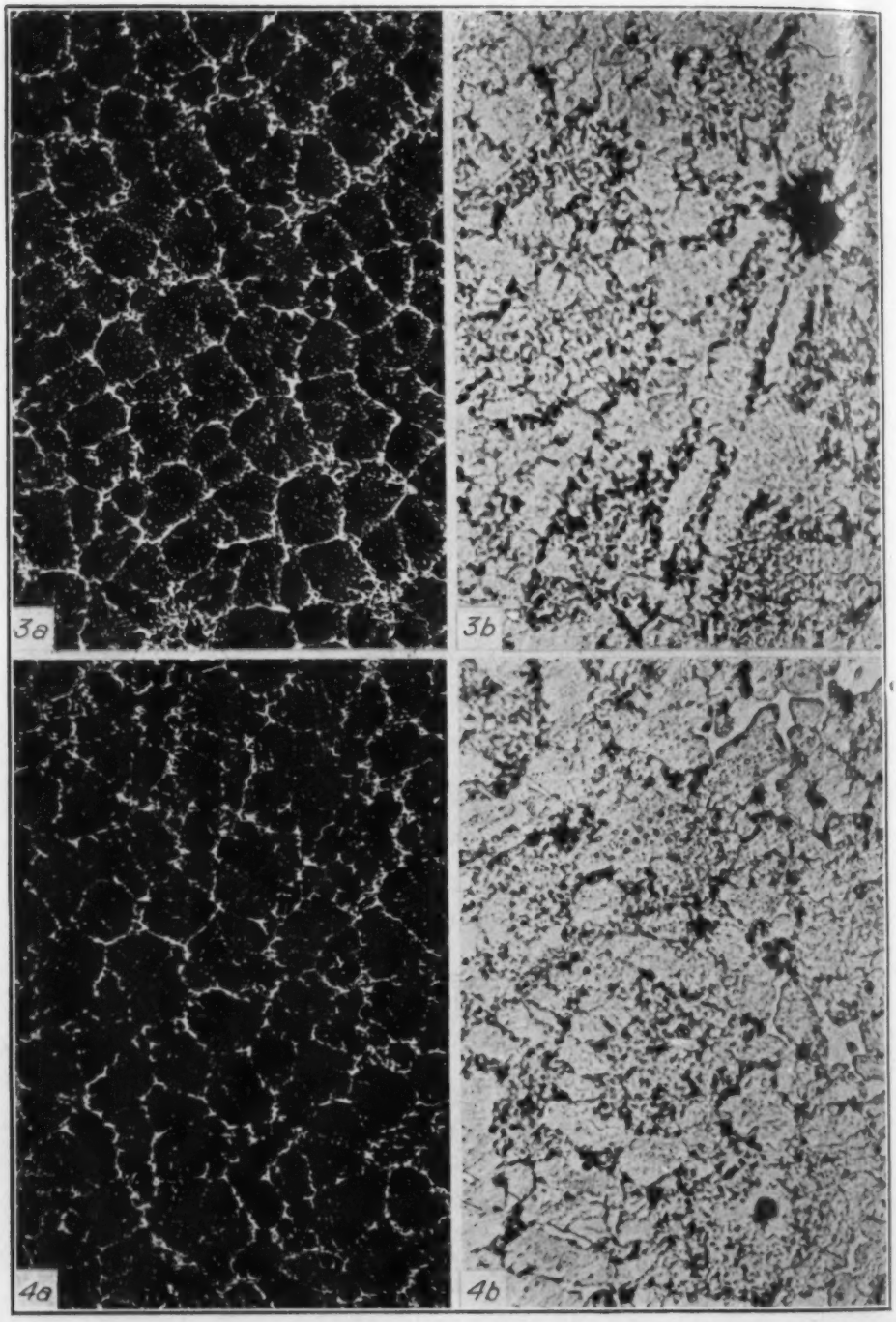


Fig. 3a—Grain-Size of Iron No. 6. Tensile Strength 41,000 Pounds Per Square Inch. × 40. Fig. 3b—Graphite Distribution of Iron No. 6. × 300. Fig. 4a—Grain-Size of Iron No. 4. Tensile Strength 53,100 Pounds Per Square Inch. Fig. 4b—Graphite Distribution of Iron No. 4. × 300.

pretation of grain-size effects in gray iron. This is perhaps more clearly shown in Fig. 5 in which the ultimate strength is plotted against the number of grains per square inch at the original magnification of the photomicrographs. The rate of increase of strength with increasing grain-size is somewhat slow at first but becomes very rapid in the coarser irons.

Another property which may be affected by grain-size variations is that of hardness. To check this point, a series of 18 piston rings was obtained in which the section size was the same. The as-cast

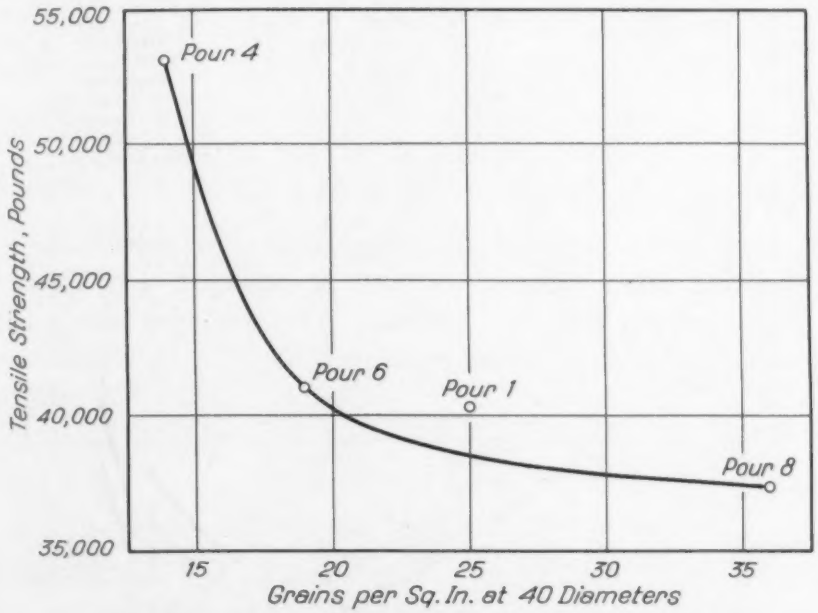


Fig. 5—Effect of Grain-Size Variation on Tensile Strength.

hardness of these rings was determined at the same location on each ring. After the standard heat treatment, samples from each ring were polished, etched and examined microscopically. The grain count per square inch at 40 diameters and the hardness are given in Table II. When the as-cast Rockwell hardness is plotted against grain count the curve of Fig. 6 results. Irons with intermediate grain-size were lacking in this series but it appears that for the size of section and the type of iron, samples with grain-sizes of 36 or over have Rockwell hardness of C26 or less while those whose grains number less than 30 per square inch at the standard magnification tend to have a hardness higher than C26. The grain-size of the cast iron has a pronounced effect upon the as-cast hardness, the hardness increasing with increasing grain-size.

Table II

Hardness Versus Grain-Size

Piston Rings			
Ring No.	Hardness Rockwell "C"	Grain-Size	Remarks
1	30	25.5	Distorted
2	29.5	26.4	Distorted
3	29	25.3	Distorted
4	28	27.0	Distorted
5	28.5	25.5	Distorted
6	27.5	28.4	Distorted
7	29	24.0	Distorted
8	28	27.0	Distorted
9	29	24.5	Distorted
10	28.5	26.2	Distorted
11	28	22.6	Distorted
12	30	26.5	Distorted
13	30	22.5	Distorted
14	27.5	26.5	Distorted
15	26	36.0	Not Distorted
16	24	39	Not Distorted
17	26	38	Not Distorted
18	26	36	Not Distorted

In Table II the ring castings are classified for distortion, namely, their deviation from flatness. It will be observed that 14 of the rings whose grain count was less than 30 per square inch are distorted while the 4 whose grain count was about 36 per square inch

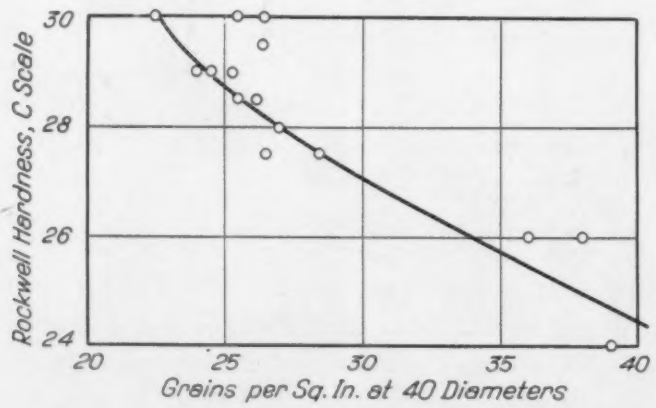


Fig. 6—Effect of Grain-Size Variation on As-Cast Hardness.

show no distortion. There is apparently a close relation between grain-size and the tendency of a casting of given section size to distort, the coarse-grained irons having a greater tendency to lose shape than do the fine-grained irons. The parallelism between grain-size effects in steel and in gray cast iron has thus far been striking.

The variation in hardness and distortion with grain-size at once suggest that hardenability experiments should prove interesting. Ac-

cordingly a bar $\frac{9}{32}$ by $\frac{1}{8}$ by 4 inch from each of the four casts whose strength properties were determined (Table I) was selected for quenching experiments. Because the cross section of the bars was such as to preclude the taking of hardness readings across the section it was decided that if one end of each bar was quenched into water an estimate might be formed as to the hardening power of each

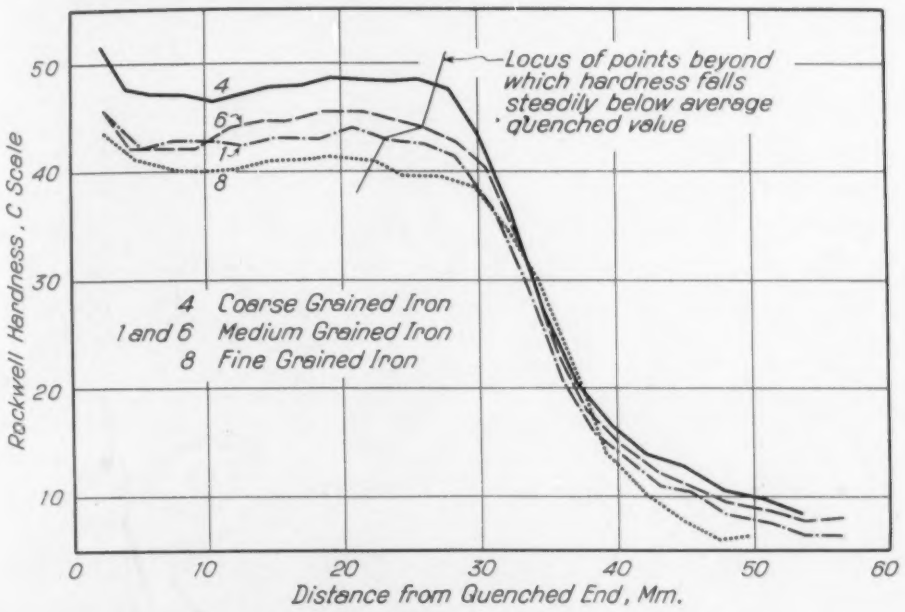


Fig. 7—Hardenability Tests on Irons 1, 4, 6 and 8.

of the four irons. Quenching was carried out in such a way that each bar was immersed to the same depth, 26.5 millimeters, in freshly drawn water and held in that position until cool. The irons were heated to about 1580 degrees Fahr. (860 degrees Cent.) for 30 minutes prior to quenching, after which the bars were ground to a uniform surface finish. Rockwell hardness readings were then taken at frequent intervals along the length of the bar beginning at the quenched end.

The results of this experiment are shown in Fig. 7 where hardness is plotted against distance from the quenched end. It will be observed first of all that the average hardness in the quenched section increased with increasing grain-size, the difference between fine and coarse-grained iron being about 6 points Rockwell C. This is a rather convincing demonstration that the hardening power varies with grain-size in gray cast iron as well as in steel. A closer examination of the curves of this figure illustrates this hardenability

Table III

Pour No.	Average Hardness Quenched Section	Distance of Point* of Decline from Quenched End, mm.	Grain Count at 40 X
8	40.3	20.6	36
1	42.3	23.3	27
6	42.9	24.9	19
4	45.5	26.6	14

*Point of decline taken as that point beyond which the hardness curve steadily declines from the average quenched hardness, i.e., it is the last point on the hardness-distance curve which has a hardness equal to the average quenched hardness.

variation in yet another way. Considering now the point beyond which the hardness begins to decline steadily from the average quenched hardness, it will be observed that these four irons suffer the break in the hardness curve at distances varying from 20.6 to 26.6 millimeters from the quenched end for the fine and coarse-grained irons respectively. The figures for the average quenched hardness, point of decline and grain-size relationship are summarized in Table III. It is very evident that the hardening power of the irons increases with increasing grain-size not only from the standpoint of the maximum hardness attained but also from that of the depth or distance to which it can be hardened under the conditions imposed.

Having observed the variations in hardenability caused by variations in grain-size in the rather crude experiments just outlined it seemed desirable to make hardenability tests of the type used by Bain and by Grossmann in their work on steel. Accordingly two bars of cast iron about $1\frac{1}{16}$ inch in diameter were obtained whose composition was nearly identical with respect to the common constituents of cast iron. The analyses of these bars, 4A and 4B, are given in Table I. The grain-size of these irons after the heat treatment previously described is shown in Figs. 8 and 9; considering the structures and analyses any variation in hardenability could reasonably be attributed to variations in the austenitic grain-size.

Sections of these bars, three or four inches long, were heated to various temperatures ranging from 1475 to 1610 degrees Fahr. (800 to 875 degrees Cent.) for one hour and then quenched in oil or water. The heat treated bars were then sectioned near the center to give a slice about $\frac{3}{8}$ inch thick. After marking off rings on one face of each slice at various distances from the center, Rockwell hardness readings were made, about 6 on each ring, and the results averaged for each ring.

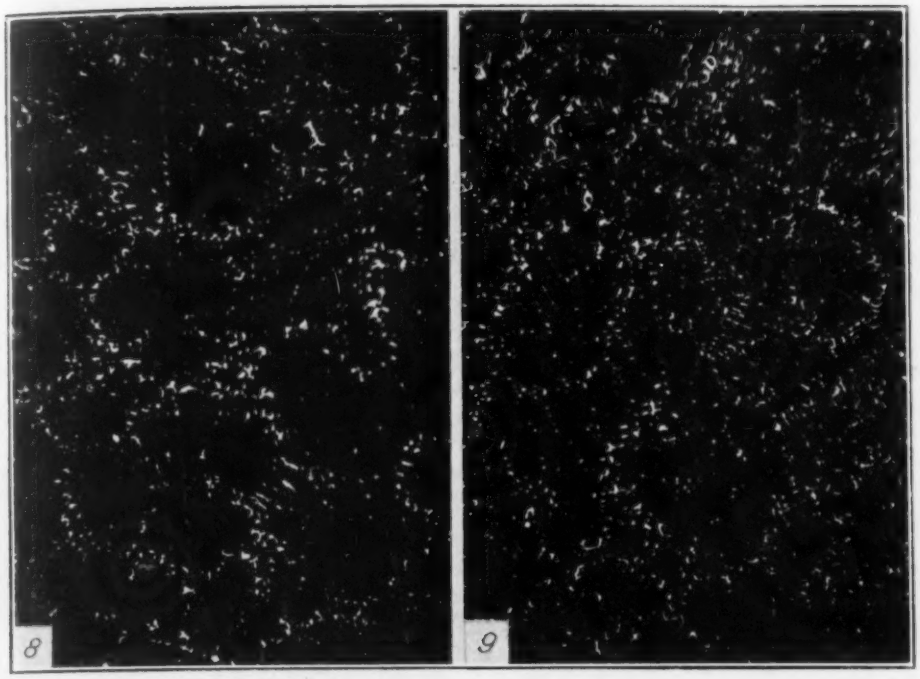


Fig. 8—Grain-Size of Iron No. 4a Used in Hardenability Tests. × 20.
Fig. 9—Grain-Size of Iron No. 4b Used in Hardenability Tests. × 20.

The results of these various experiments are shown graphically in Fig. 10. It is quite evident that even in the samples quenched from 1610 degrees Fahr. (875 degrees Cent.) the two irons behave differently in hardening. The coarse-grained iron for all practical purposes hardens throughout its section while the fine-grained iron hardens only to a depth of $\frac{1}{8}$ inch. It is also observed that the fine-grained iron does not attain as high a hardness as the coarse-grained material. The samples quenched from 1525 degrees Fahr. (830 degrees Cent.) into water show a lower hardness and a more pronounced difference between the coarse- and fine-grained irons. The coarser iron hardens practically completely although there is, to be sure, some drop in hardness toward the center. The fine-grained iron, however, in addition to a somewhat lower maximum hardness also shows a pronounced decrease in hardness toward the center. In fact it hardens to a depth of $\frac{1}{16}$ inch only.

When bars are quenched from 1525 degrees Fahr. (830 degrees Cent.) into oil the maximum hardness attained is lower than for water quenching and both irons show a decrease in hardness toward the center. Here again the coarse-grained iron is higher in hardness

particularly at the center, than the fine-grained iron. There is in all of these curves a striking similarity to the results obtained with coarse- and fine-grained steels. It seems reasonable, therefore, to observe that to heat treat gray cast iron with uniform results it will be necessary to control the austenitic grain-size of the iron.

The implications of the variations in hardenability as it affects other properties are clear when it is considered that the casting opera-

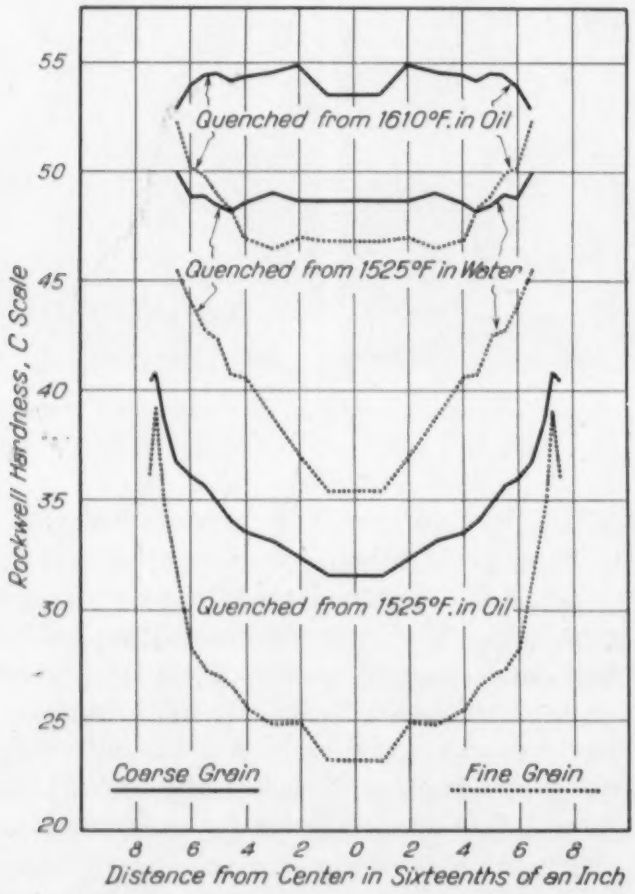


Fig. 10—Hardening Tests on 1⅛ Inch Round Bars.

tion is at least a partial quench. If this is admitted, then it is possible that the variations in hardness and strength of the as-cast samples due to grain-size differences are a direct result of the influences of grain-size on hardenability. Furthermore, on the basis of the hardenability results presented, it would seem reasonable to expect considerable variation in the as-cast properties even in comparatively large sections if the austenitic grain-size varies widely, since we have ob-

served that the fine-grained irons do not produce a hardness equivalent to that of the coarse-grained irons even under rather drastic quenching conditions.

Consideration of the facts brought out in this work lead to many interesting speculations. It is entirely plausible that grain-size variations have produced in past researches on cast iron and in its commercial production an elusive and seemingly irrelevant variation in properties. Grain-size characteristics which have explained so well the present case seem to furnish an additional tool not only for research, but also for commercial control of properties. As such it may perhaps throw further light on the complex material known as cast iron and in the end simplify the production of metal of a high degree of uniformity. These tests have also supported with considerable force the growing belief that ordinary chemical specifications for cast iron mean relatively little. Specifications of physical properties may also prove to be inadequate for many applications in the light of future research.

The question of hardenability seems destined to play a more and more important part as the advantages of heat treated cast iron become more widely appreciated. As heat treating of cast iron becomes more widely used, an adequate and thorough knowledge of the hardenability of cast iron will be necessary and as in the case of steel one of the best avenues of approach is that of grain-size control. It should not be difficult to predict, in view of the parallelism of steel and cast iron, that the development of methods of control of this factor should lead to a much wider appreciation of unalloyed gray cast iron and to a more efficient use of alloy materials.

It is readily admitted that many questions are left untouched in the present report. Among these are the effects of alloying elements on grain-size, the effects of variation of size of section, the effects of various factors in melting operations, the question of coarsening temperatures, the effects of time at temperature (in the solid state), the relationship between graphite distribution, grain-size and physical properties. It has been the aim of this paper to stimulate thought in this direction with the expectation that further work in this field should lead to interesting and valuable information regarding the manufacture and utilization of gray cast iron.

To summarize the work thus far, the following conclusions may be drawn:

(1) That in irons of approximately constant graphite char-

acteristics and chemical composition wide variations in physical properties may be due to austenitic grain-size variations.

(2) That austenitic grain-size characteristics affect powerfully the strength, hardness, distortion and hardenability of cast iron.

(3) That as the austenitic grain-size increases the as-cast strength and hardness and the distortion increase, probably because of the increased hardenability of the coarser-grained irons.

(4) That control of grain-size in cast iron should lead to important advances in the art of its heat treatment, to a better understanding of both unalloyed and alloyed cast iron and to a more efficient use of both types.

ACKNOWLEDGMENT

The authors desire to express their appreciation of the co-operation of Neil A. Moore, of the Sealed Power Corporation, who furnished the irons for part of this study and to Professor A. E. White, of the Department of Engineering Research of the University of Michigan, who has acted as friend and advisor in this work.

DISCUSSION

Written Discussion: By V. A. Crosby, Climax Molybdenum Co., Detroit.

I was much impressed with the remarkable increase in strength values from the base iron and, to all intents, the same procedure employed in melting, pouring, etc. The analyses shown are practically identical.

It is regrettable that the unetched photomicrographs showing the graphite size and distribution are rather indistinct—especially in view of the fact that, all other factors being equal, we recognize the great importance of this phase in cast iron.

I do not feel that one is justified in drawing conclusions from such a few samples investigated. I am constrained to believe that the differences in physical properties are entirely too great to be attributed to grain-size alone. We are well aware of the fact that should there be no graphite in the samples investigated, thus eliminating the graphite phase altogether, there would only be approximately a few thousand pounds strength difference between a No. 2 and a No. 6 grain-size steel casting, whilst the grain-size-tensile strength curve as shown on page 81, when converted from 40 to 100 magnification and using the McQuaid-Ehn count, indicates a No. 2 for the coarse and a No. 4 for the fine grain, and with this small difference in grain-size an increase of 40 per cent in strength is observed.

The method of determining the grain outline is rather indirect and while

not necessarily incorrect is open to question. However, we are indebted to Mr. Murphy for this method of preparing the specimen.

The statement made with reference to the effect of grain-size on distortion is very interesting and one, I am sure, worthy of further consideration, especially since this is a problem of no mean proportion in most foundries.

The hardenability characteristics of fine- and coarse-grained cast irons as mentioned indicate close similarity to steels of various grain-size. In fact, this argument seems to be the most convincing that the subject under consideration is austenitic grain-size.

My own experience with irons of 30,000-45,000 pounds per square inch indicates no difference in grain-size, but rather the difference could be traced to graphite distribution and matrix characteristics.

Cell structure in gray cast irons has been observed for several years and known as phosphide or carbide network and, in more recent times, as a ferrite fine graphite boundary line network. The latter is said to be caused by certain alloy additions.

Written Discussion: By A. I. Krynitsky, associate metallurgist, National Bureau of Standards, Washington, D. C.

In the opinion of the writer, this paper is a valuable contribution to the study of the structure of cast iron and the authors should be congratulated for the development and application of a method by which austenitic structure may be revealed.

It may be expected, of course, that cast iron "will be affected by the same variables in the same manner as is steel."

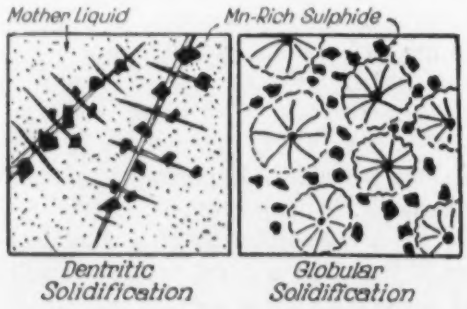
There are, however, some points which, in the writer's opinion, warrant discussion.

The problem studied by the authors involves so many factors that it is very difficult to keep all possible variables constant but one. Assuming that the matrix of the specimens investigated was approximately the same and that graphite particles were of the same size and similarly arranged, we still should not overlook another possible factor which, in the opinion of the writer, probably is as important as austenitic grain-size. This factor is the primary structure. By the term "primary structure" is meant the structure which is formed during solidification and not the structure of fractured sections. Examination of fractures, as Roll[1] states, does not permit drawing any definite conclusion regarding the mode of crystallization. The primary structure is masked by changes during transformations on the cooling of the metal from the solidus to room temperatures. It may, however, be revealed by Baumann's sulphur print method or by other suitable methods to supersede examination of the structure of fractured sections. Manganese-rich sulphides solidify at a temperature above the solidus and are dispersed throughout the mass of molten cast iron. Upon solidification of the iron, the manganese sulphide particles arrange themselves along the axes and branches of dendrites or the boundaries of grains as illustrated in the diagrammatic sketch shown in this discussion which characterize the two types of primary crystallization occurring in cast iron. Roll took advantage of the arrangement of the man-

[1]Franz Roll, "Das Primärgefüge des grauen Gusseisens," *Archiv für das Eisenhüttenwesen*, Vol. 8, No. 3, September 1934, p. 129-130.

ganese sulphide particles to show by means of sulphur prints not only the type but also the size of the primary crystals. It is believed that further study of the problem presented by the authors along the line of establishing a relationship between the type and perhaps size of primary crystals with the austenitic grain-size would be of value and interest.

Referring to the type of graphite arrangement in irons, illustrated in the paper in Figs. 1b to 4b inclusive, the writer does not fully agree with the authors' interpretation. It appears that the structures shown in Figs. 1b and 2b are more or less similar, whereas the photomicrographs presented in Figs. 3b and 4b indicate the presence of coarse dendrites.



Diagrammatic Sketch Illustrating Arrangement of Manganese Sulphide Particles During Solidification of Cast Iron as Shown by Franz Roll.

In this connection and without an attempt to draw any conclusions it may be of interest to mention that in the tests conducted at the National Bureau of Standards it was observed by the sulphur print method that iron of the composition, 3.79 per cent total carbon, 1.32 per cent silicon, 0.06 per cent sulphur, 0.75 per cent manganese and 0.12 per cent phosphorus, superheated to 1700 degrees Cent. was markedly different in its primary structure from the same iron heated to lower maximum heating temperatures. The iron heated at 1700 degrees Cent. had a pronounced acicular structure and possessed greater strength than the same iron heated to lower maximum heating temperatures.

Written Discussion: By F. G. Sefing and M. F. Surls, Michigan State College, E. Lansing, Michigan.

The authors are to be commended for presenting the idea of a relation between the physical properties of cast iron and the metallurgical structure. The writers have tried the procedure outlined by the authors to develop the grain-size on several cast irons with 3.25 per cent carbon and 2.25 per cent silicon, but without any success whatever. In fact the results obtained had some semblance to the rather vague grain-size of Fig. 9 of the paper, but it was impossible to discern any grain outlines.

We should like to ask the authors some questions pertaining to the photomicrographs.

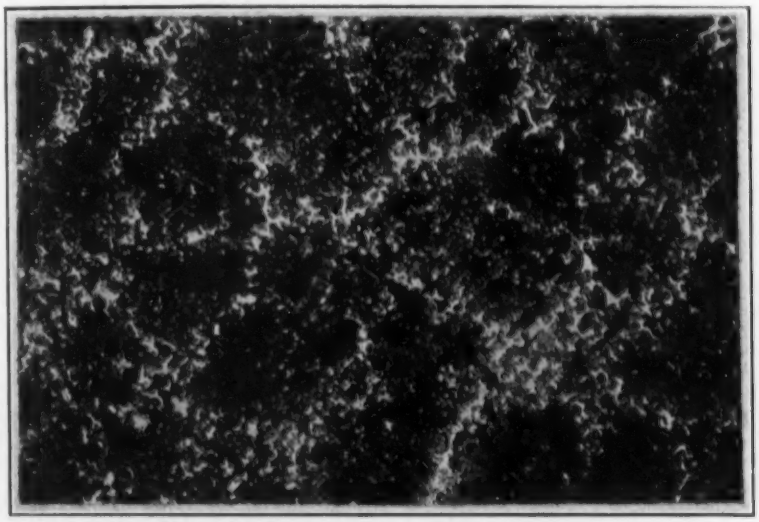
1. What are the light and dark constituents of Figs. 1a, 2a, 3a, 4a, 8 and 9?

2. Why should the outline of light and dark areas of the above figures be called the austenitic grain boundaries?

Written Discussion: By A. L. Boegehold, General Motors Co., Detroit.

The description of tests made by the authors makes it appear quite likely that cast irons vary in their hardenability in a manner quite similar to variations in steel. The writer can think of no reason why this should not be so. It does not seem, however, that the evidence presented shows very well that the variation in degree of hardenability is related to austenitic grain-size.

It is not clear that structures shown in Figs. 1a, 2a, 3a, and 4a indicate austenitic grain-size. The corresponding photomicrographs 1b, 2b, 3b, and 4b contain fragments of carbides which would indicate to one familiar with these structures that the network structure shown at low magnification is made up by the arrangement of the carbides shown in detail in the photomicrographs at 300 diameters. The location and size of such a network is es-



Structure of a 5-Inch Diesel Engine Piston Ring Casting Etched in Nitric Acid. C 3.62, Si 2.63, Mn 0.59, P 0.287, S 0.072. Brinell Number 255-269. × 75.

tablished at the eutectic freezing temperature and is not changed by heating to 1650 degrees Fahr. (900 degrees Cent.). This type of structure has been frequently observed by the writer and it is not necessary to use other than the regular nitric acid etch to bring it out and the accompanying photomicrograph shows such a structure brought out by nitric acid etch. This structure was observed in a piston ring containing about the composition given by the authors and cast in sections similar to that of the authors' test bars. It is unfortunate that more complete chemical composition of the cast irons studied was not given in the paper.

The network structure in piston rings usually contains a considerable amount of phosphorus which would render the network immune to any change by heating to a temperature of 1650 degrees Fahr. (900 degrees Cent.), as done by the authors. If no phosphide was present in such a network, heating to 1650 degrees Fahr. (900 degrees Cent.) would in all probability have the

effect of decomposing the iron carbide in the presence of 2.90 per cent silicon, such as contained in the authors' cast iron. Any carbide dissolved by heating to 1650 degrees Fahr. (900 degrees Cent.) would probably precipitate as proeutectoid cementite upon cooling and this proeutectoid cementite would outline the true austenitic grain-size within the network structure formed at the eutectic freezing point. A suggestion of such a secondary formation of carbide precipitated as proeutectoid cementite may be seen in the authors' photomicrographs Figs. 3a and 4a.

The authors attribute the variation in strength to the difference in austenitic grain-size of the irons studied, having decided that the graphite size and distribution and condition of the matrix as being the same in all cases. The photomicrographs on pages 79 and 80 at 300 diameters are unsuitable for judging the condition of the graphite size and distribution and do not show what the matrix condition is. If one were to hazard a guess as to the graphite distribution, it would be that the size of the graphite was not similar in the four irons. It would have been very desirable to include in this paper some photomicrographs of the condition of microstructure before it was heated to 1650 degrees Fahr. (900 degrees Cent.) at magnifications suitable for observing graphite size and distribution and nature of the matrix. Experience in examining many examples of cast iron similar to those under discussion would lead the writer to expect that such a picture would show the same network structure as shown after heating to 1650 degrees Fahr. (900 degrees Cent.).

Although the authors' connection between austenitic grain-size and hardenability seems very tenuous, the important point after all is the fact that cast irons do exhibit differences in hardenability just as observed in steels and the authors are to be congratulated for presenting this point.

Oral Discussion

J. S. VANICK:[2] Some of the questions that occur to my mind in going over this paper have already been raised in written discussion. The first point involves the question as to whether these are actually austenite grains, for the reason that grains in any cast iron are very difficult to outline. We are all familiar with the solidification pattern of noncrystalline materials and that type of solidifications may be compared to the hexagonal soap-bubble pattern for instance, which has no crystallographic origin so far as we know, yet it does form a crystalline pattern. We have frequently observed in cast iron a cellular pattern in microstructure as well as in fracture, sometimes to our hope and sometimes to our dismay depending upon whether the outline was ferritic or cementitic but it has been difficult to identify it as an austenitic grain outline. I would like to put the question to the authors as to whether this condition has been observed in any irons other than the one described or in sections other than those described here, because the grain-size would depend much upon solidification rates and cooling conditions.

The next question I have is in regard to page 78 of the paper, where reference is made to the strength of a high silicon high carbon iron at 53,000 pounds per square inch. I think that would be worth clearing up to the extent of indicating that it was probably measured on a very small piston ring

[2]International Nickel Co., Bayonne, N. J.

section. Otherwise, it is liable to become confused in the mind of foundrymen as something that is obtainable in the ordinary standard test bars. The next point I have in mind is a relatively small difference for these rather wide differences in grain-size, that is, the strength change from 40 grains per square inch of 37,000 pounds per square inch to a level of 40,000 pounds per square inch, where the grains are just half the size. It seems to indicate that the grain-size in that particular range is not a very vital factor. The rapid jump to 53,000 pounds per square inch for a smaller grain count would seem to indicate that some unobserved factor is taking part in the effect. I would like to emphasize that it would be a difficult thing to control either cell or grain-size, and I am aware that the authors do not offer any solution to the problem, so that until we have more information on how this might be achieved, foundrymen will naturally be compelled to follow more simple procedures in bringing up their strength hardenability, and other important physical properties.

Authors' Oral Closure

By P. W. Wood

Mr. Murphy and I appreciate very much the written discussions that have been submitted as well as the various oral discussions that we have had. I think we should emphasize what was possibly intimated in the paper, that our idea in presenting this material was largely to provoke discussion since having run across this rather interesting variation of properties, we thought it worthwhile to discuss it, and see if others had some ideas about it. In regard to Mr. Boegehold's discussion, and one of the other discussions which were not read, the mention of the existence of phosphide in this network was brought up, and the impression was given that possibly the network was produced by precipitation of phosphide. It is a little difficult to see how with such little variation in phosphorus content of the iron there might be such a variation in the network produced, because it would necessitate in the fine-grained irons (if we may call them that) a considerably greater amount of phosphide. In the first four irons that were shown after the heat treatments have been applied, there seems to be an increased precipitation in the original network. We still have the question, granting that it might be phosphide which gives us this network—why should the phosphide arrange itself in varying size of mesh in the pattern, and why should we have these rather striking differences in the physical property? I do not think that either Mr. Murphy or myself are ready to take oath that this is absolutely austenitic grain-size, but we were more or less forced to that decision, particularly when viewing the hardenability curves as giving results which seem in accordance with the variations in grain-size, as we call them. Another point in Mr. Boegehold's discussion about the photomicrographs on pages 79 and 80 showing the graphite distribution, these irons were in the as-cast condition—that is, they had not been subject to any heat treatment in order to bring out the network structure.

In regard to Mr. Krynitsky's discussion we have not had an opportunity to check Mr. Roll's article, and we would rather withhold any comment until we have had such an opportunity. With regard to Messrs. Sefing's and Surl's questions on the photomicrograph showing the network structure,

we feel that it is quite probable that considering the iron we have there, it is possibly ferrite and possibly some phosphide. The dark constituent is possibly the unresolved constituent of the iron, due to the low magnification that was used; probably some sorbitic structure there.

Going back to the question of phosphorus, when we made the last test (the hardenability test) the phosphorus content in that iron was very low, 0.018 per cent. We made another observation on iron which contained 0.04 per cent phosphorus, and were still able to produce the network structure. I can hardly see with 0.04 or 0.018 per cent phosphorus how the phosphide idea would account altogether for the network absorbed.

Authors' Written Closure

We appreciate very much the discussions which have been submitted in connection with this paper.

One point which was mentioned in several of the discussions was that the network structure observed was due to the precipitation of iron phosphide. The authors do not believe that this network is entirely due to phosphide, for the reason that it would be logical to expect a considerably higher phosphorus content in the fine-grained irons as compared to the coarse-grained irons. These irons all had a uniform phosphorus content of about 0.5 per cent. It is our opinion that the network in these irons is made up of ferrite and iron phosphide. The matrix is probably sorbitic due to the heat treatment. We have observed a network structure in the as-cast condition similar to the photomicrograph presented by Mr. Boegehold in his discussion. It is our opinion that a heat treatment of this type of iron serves to accentuate the network structure which may already be present in the as-cast condition.

Since the work reported in this paper, further study has been made of a series of cast irons of the following composition, the metal being cast into bars with a diameter of 2.5 inches: Total carbon 2.60, silicon 2.55, sulphur 0.018, phosphorus 0.041, other alloying elements 3.50.

To develop a network structure in this iron it was necessary to use a heat treatment consisting of heating to a temperature of 1800 degrees Fahr. for 75 minutes, cooling to 1300 degrees Fahr. in a second furnace, holding at 1300 degrees Fahr. for 20-30 minutes and quenching into water. The samples were then drawn at about 1000 degrees Fahr. and prepared for microscopic examination. It will be observed that this heat treatment is quite similar to that found so useful by those studying grain-size effects in steel. The resulting structure is shown in Fig. 1 (of this closure), nital being used as an etchant. For comparison, the same iron was treated in the same manner, except that a maximum temperature of 1600 degrees Fahr. was used instead of 1800 degrees Fahr. Fig. 2 shows the structure of the iron after this heat treatment. It is obvious that the higher temperature has affected the iron in such a way as to reveal a network structure very clearly.

The question raised by Mr. Vanick as to whether or not similar structures had been encountered in other irons than those described in the paper seems to us to be sufficiently answered by the example just cited. In the

case of this iron we observed no network structure in the as-cast condition; in fact, we found it practically impossible to reveal this structure clearly at any heat treating temperature below 1800 degrees Fahr. as the photomicrographs show. As a further conclusion from these later experiments, and in view of the extremely low phosphorus content of the iron, we believe that the ability of an iron to show a network structure is not greatly dependent on the phosphorus content of the iron. It seems to us that any cast iron may be

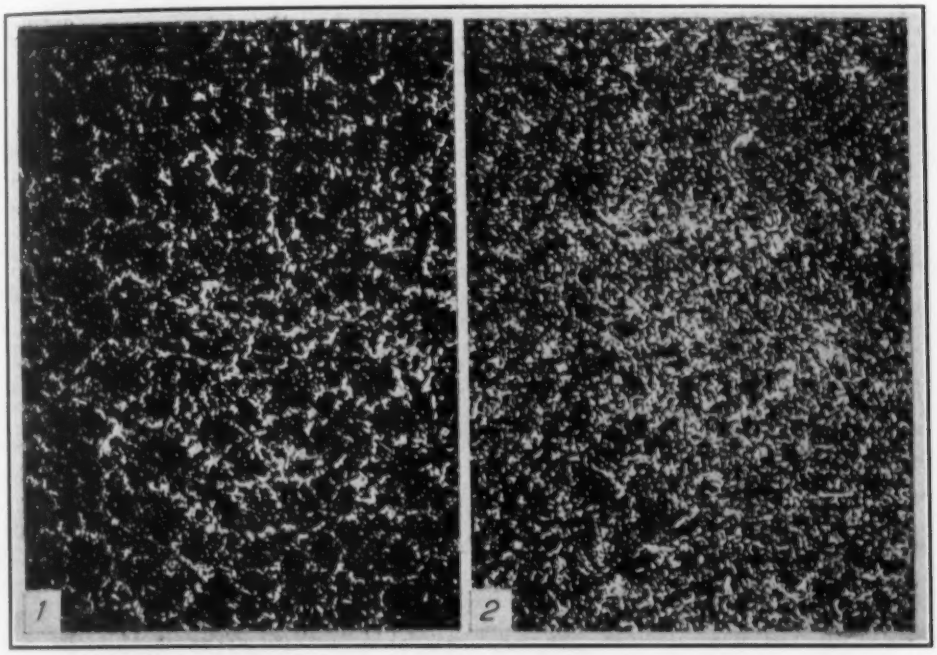


Fig. 1—Cast Iron Heated at 1800 Degrees Fahr. for 75 Minutes; Cooled to 1300 Degrees Fahr. and Held for 25 Minutes; Water Quenched; Drawn at 1000 Degrees Fahr. for 20 Minutes. Etched with 4 Per Cent Nital. × 7.

Fig. 2—Cast Iron Heated at 1600 Degrees Fahr. for 75 Minutes; Cooled to 1300 Degrees Fahr. and Held for 25 Minutes; Water Quenched; Drawn at 1000 Degrees Fahr. for 20 Minutes. Etched with 4 Per Cent Nital. × 7.

caused to show its network or austenitic grain structure, provided the proper heat treatment can be developed.

Mr. Krynitsky has raised a question with regard to the relationship of the primary structure as discussed by Roll and the austenitic grain structure as presented in this paper. At this time we are unable to link his observations with our findings and we feel, as does Mr. Krynitsky, that future research combining the two methods of attack may provide much useful information.

At the present time, we do not feel that the data are sufficiently conclusive to warrant a positive statement that the structures we have observed are those of the austenitic grains. And yet no alternative explanation has served as well to correlate our observations on physical properties, hardenability, and structure.

GRAIN-SIZE AND ITS INFLUENCE ON SURFACE DECARBURIZATION OF STEEL

By D. H. Rowland and Clair Upthegrove

Abstract

The authors in this paper set forth the results of their study of the effect of grain-size on the surface decarburization of steel by moist hydrogen. The tests were confined to carbon steels ranging in carbon content from 0.71 to 1.07 per cent. The data obtained indicates that grain-size influences the rate of carbon removal from steel.

The effect of time and temperature on the character and width of the ferrite band for coarse- and fine-grained steels was determined and the results tabulated.

Columnar grain growth above and below the gamma to alpha change point is given consideration and a theory advanced to explain the mechanism of ferrite columnarization below the A_1 point.

The gaseous products of decarburization were analyzed and an explanation of the mechanism of decarburization put forward.

Introduction

PUBLISHED data concerning the surface decarburization of steel at elevated temperatures by certain gases have been remarkably contradictory; especially those dealing with hydrogen as the decarburizing agent. Austin (1)[1], in accounting for the failure of different workers in obtaining agreement, has, quite logically, suggested a number of factors which throw some light upon the situation, namely: the varying purity of the gases employed; time factor in experimentation, and the technique used in determining carbon elimination.

There is little to be found in the literature relative to the possible

Based on a dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the University of Michigan.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. Of the authors, D. H. Rowland is graduate student, Department of Chemical and Metallurgical Engineering at the University of Michigan, and Clair Upthegrove is Professor of Metallurgical Engineering, Department of Chemical and Metallurgical Engineering at the University of Michigan, Ann Arbor, Michigan. Manuscript received June 1, 1935.

Table I

Composition of Steels Investigated

Steel No.	Per Cent				
	Carbon	Manganese	Phosphorus	Sulphur	Silicon
1	0.71	0.40	0.015	0.028	0.21
2	0.76	0.43	0.017	0.028	0.19
3	0.76	0.54	0.018	0.030	0.16
4	0.71	0.50	0.015	0.033	0.11
5	0.76	0.50	0.020	0.027	0.19
6	0.77	0.68	0.020	0.028	0.21
7	0.96	0.40	0.027	0.035	0.36
8	0.93	0.73	0.025	0.036	0.21
9	1.01	0.38	0.012	0.029	0.137
10	0.99	0.42	0.021	0.035	0.16
11	1.02	0.45	0.018	0.026	0.058
12	1.07	0.37	0.018	0.038	0.39

effect of grain-size on the rate of carbon removal from steels. Various observers have reported that some steels, when subjected to drastic decarburizing conditions, develop a ferrite band in which the grains are columnar, while other steels show an equiaxed structure in this area. Several theories have been advanced to explain the columnarization of the ferrite in the totally decarburized zone, but its possible bearing on the rate of decarburization, when compared with that which would take place if the crystals in this region were equiaxed, appears to have been more or less ignored.

Because of the increasing emphasis being placed on the influence of grain-size in heat treating operations, a series of tests were conducted for the purpose of determining whether or not grain-size and configuration affect the rate of surface decarburization by gases—that is, given two specimens of steel containing substantially identical percentages of C, Mn, Si, S and P, would the two be decarburized to a like degree if one were an inherently fine-grained steel and the other an inherently coarse-grained steel, other conditions being equal? If the degree of decarburization were unequal for the two samples under consideration, would the analyses of the gaseous products of the decarburization process indicate this difference?

It was believed that the data thus obtained would give further insight into the mechanism of decarburization.

Materials

The analyses of the twelve steels used in this investigation are given in Table I. As received, they were in the form of forged

rounds, numbers 1, 2 and 3 being 1⅛ inches, and the remainder 1 inch in diameter.

Specimens 6 inches long were turned from the forged stock, after normalizing, down to a diameter of ⅞ inch in order to remove any decarburized area, and to provide original centers for concentric turnings subsequently to be taken for carbon determinations. After tapping one end of each to a depth of about ¼-inch, to take a $\frac{3}{16}$-inch threaded rod, they were polished with No. 0 emery cloth and washed with ether before being placed in the decarburizing furnace.

Grain-Size

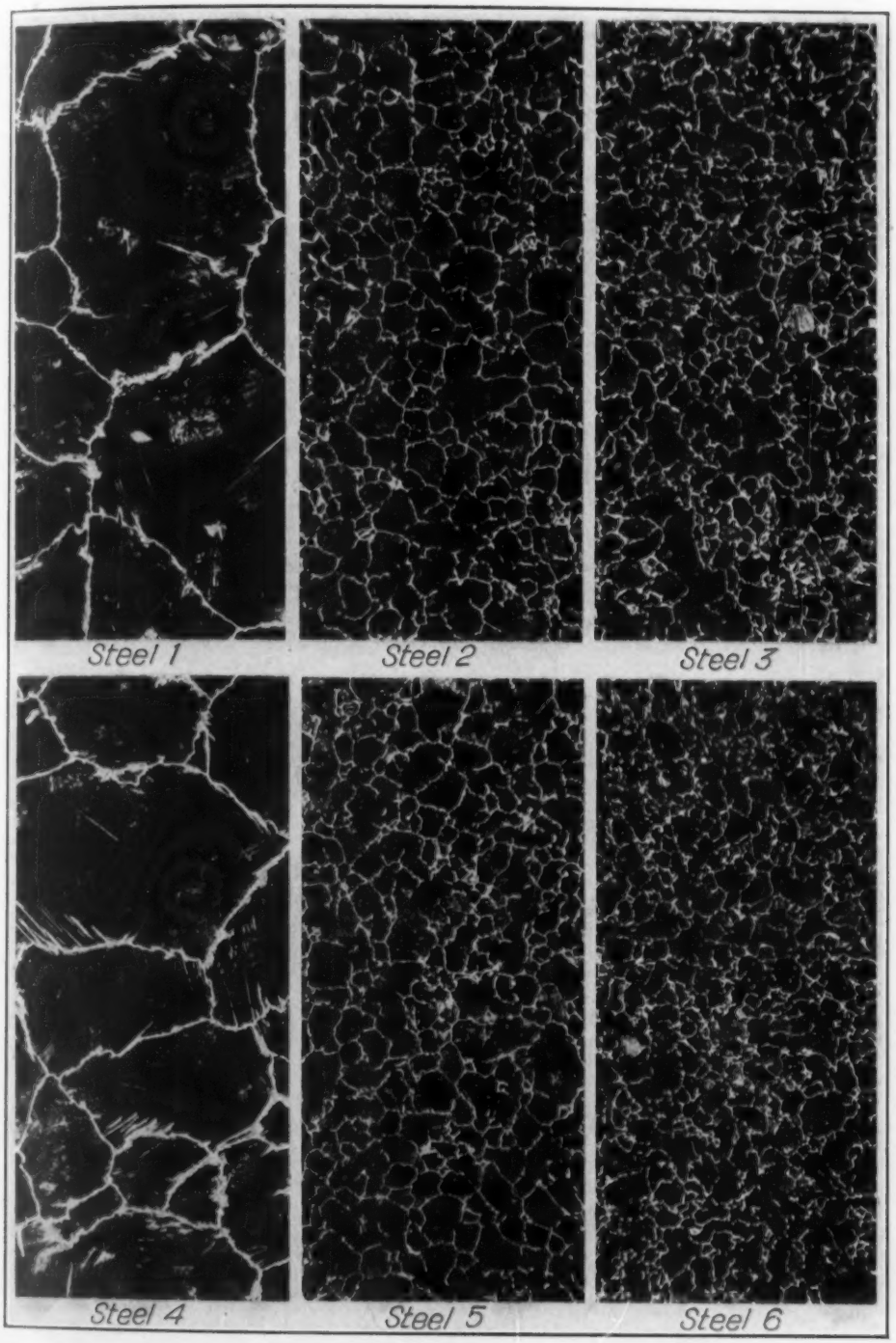
Insofar as this investigation is concerned, two types of grain-size were determined—inherent and actual. The first was revealed through the McQuaid-Ehn test as given in the following tabulation.

Steel No.	McQuaid-Ehn Grain-Size
1	1
2	6
3	7
4	1
5	6
6	7
7	5
8	7
9	1–4
10	2
11	1–5
12	3

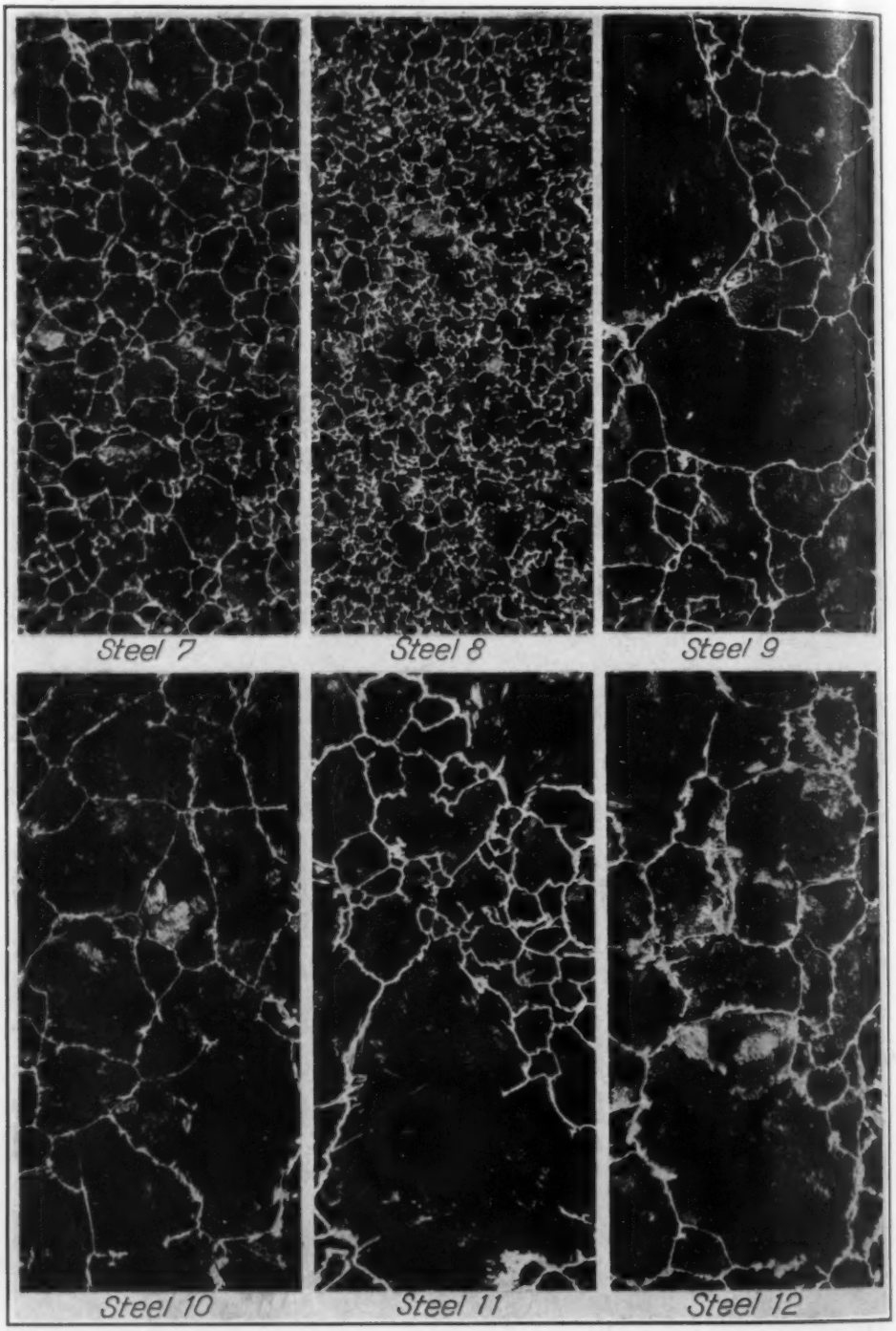
The actual grain-size, or that existent at any particular decarburizing temperature, was obtained by quenching sections large enough so that at some point in them the cooling rate would be slightly less than the critical quenching speed. Figs. 13 to 16 are indicative of some of the results brought about by this procedure. Due to relatively low quenching temperatures the grain-size at 100 diameters was somewhat indefinite, necessitating the use of a higher magnification. The grain-size of 1300 degrees Fahr. (705 degrees Cent.) was taken to be that resulting from the normalizing treatment.

Experimental Apparatus

The experimental set-up, which is a modification of the apparatus employed by Austin (1), is shown in Figs. 1 and 2. The hydrogen gas, containing small amounts of free oxygen, nitrogen



Grain-Size of Steels 1 to 6 as Revealed by the McQuaid-Ehn Test. × 100.



Grain-Size of Steels 7 to 12 as Revealed by the McQuaid-Ehn Test. × 100.

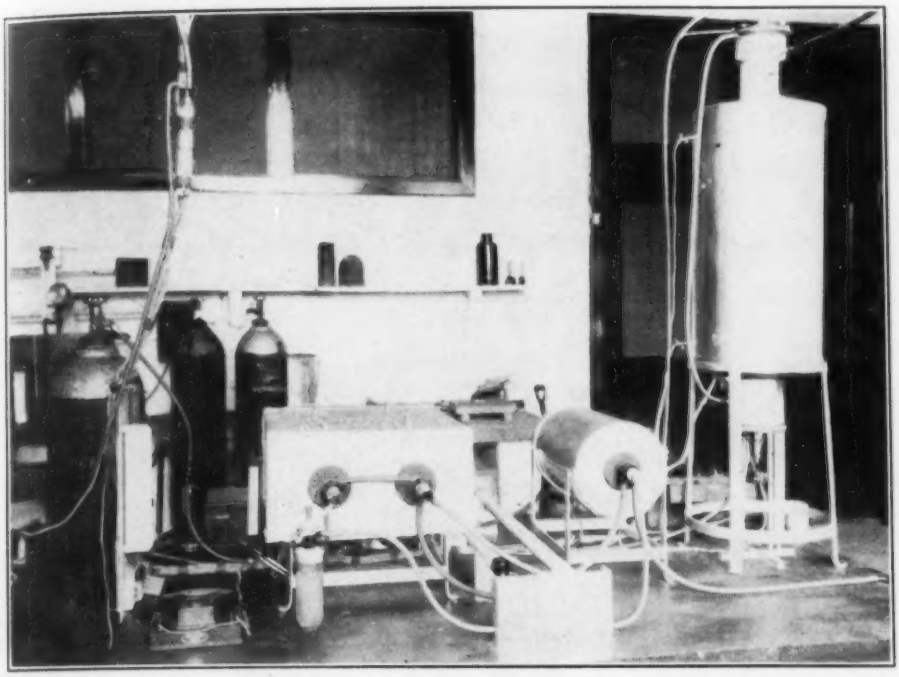


Fig. 1—Photograph of Experimental Apparatus.

and water vapor, was supplied from a cylinder 1. The manometer 2 served as a safety valve, should the line become plugged, and to aid in the regulation of the gas flow. The first step in the purification of the tank hydrogen was to pass it through a furnace 3 filled with platinized asbestos heated to about 950 degrees Fahr. (510 degrees Cent.) thus effecting the combination of free oxygen. The water formed, together with that originally present, was removed by activated alumina 4 and phosphorus pentoxide 5. After drying, the hydrogen was essentially free from impurities excepting nitrogen, the presence of which was not considered of sufficient importance to warrant its removal. As a check on the purity of the gas at this stage, it was by-passed by means of a three-way cock 6, before and after each run, for a period of one hour, through a furnace 7 containing a strip of polished stainless steel heated to 1300 degrees Fahr. (705 degrees Cent.). Austin (1) has previously commented upon the use of stainless steel as a means of detecting traces of water vapor and oxygen in hydrogen.

On the way to the decarburizing furnace 8 the purified hydrogen is next led over an electrolytic cell 9 containing as an electrolyte a 10 per cent aqueous solution of potassium hydroxide where it picks

up a calculated amount of electrolytic hydrogen and oxygen which, when recombined to water, will saturate it at room temperature. Finally, the gas was passed through a furnace 10 filled with copper gauze at 950 degrees Fahr. (510 degrees Cent.). Here the hydrogen and oxygen from the cell is catalyzed to water vapor. The three-way cock 11 permitted a checking of the water content of the hydrogen before it entered the decarburizing chamber. The calibrated flow

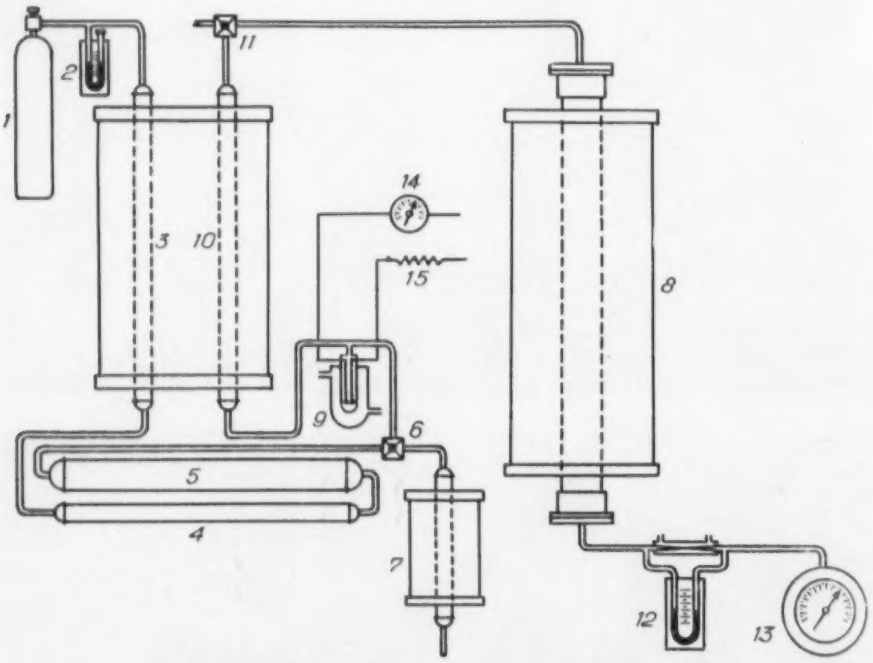


Fig. 2—Schematic Diagram of Experimental Apparatus.

meter 12 indicated the flow rate, and the meter 13 measured the volume of gas passed through it during a decarburizing period.

The reason for the removal of the water vapor and free oxygen from the tank hydrogen was twofold. First, it facilitated calculations with regard to the electrolytic cell, the hydrogen and oxygen from which, of course, depends upon the current flowing in the circuit. Knowing the volume of dry hydrogen passing through the system per hour, the water required to saturate it can be procured by calculating the current theoretically necessary to liberate an equivalent amount of hydrogen and oxygen. The cell, when prevented from heating up by the use of a water jacket in which the water was kept circulating, was practically 100 per cent efficient. The nickel electrodes of the cell were connected through a milliammeter

14 and rheostat 15 to a 110-volt direct current line. The second use for dry hydrogen was to provide a heating and soaking atmosphere in which the extent of decarburization would be negligible (Austin 1).

In carrying out the experimental work, three specimens of different grain-size were always run simultaneously. This was done in order to subject each of the three to identical conditions. To this

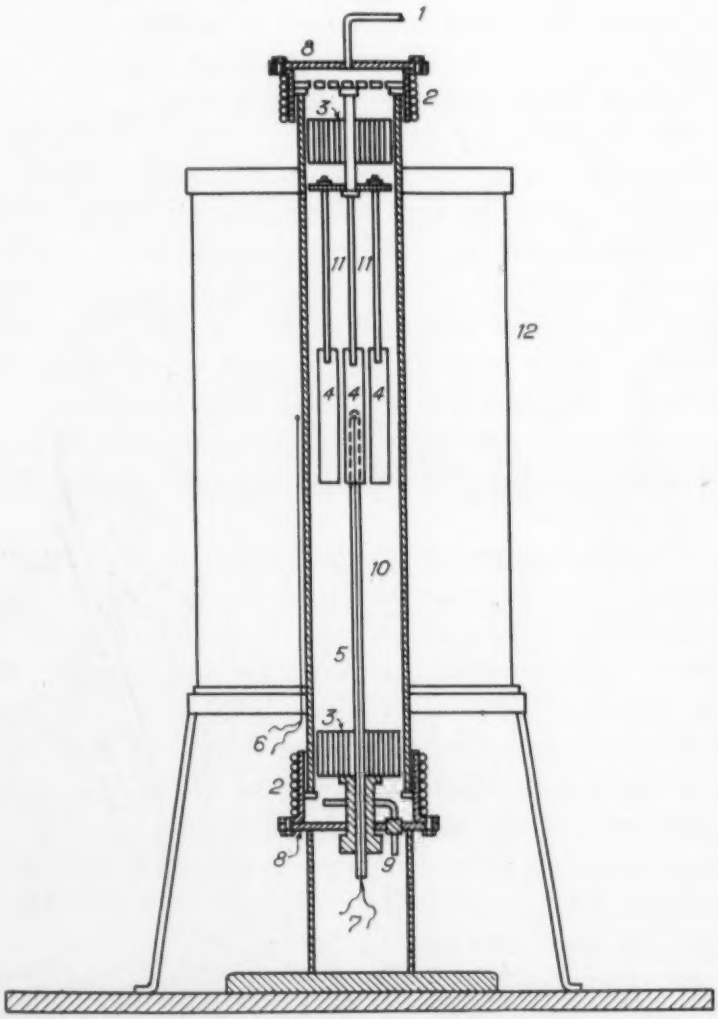


Fig. 3—Details of the Furnace in Which Specimens Were Decarburized.

1. Gas Inlet
2. Water Cooling Coil
3. Sil-O-Cel Plug
4. Specimens
5. Thermocouple Shield
6. Check Thermocouple to Potentiometer
7. Control Thermocouple
8. Steel Caps
9. Gas Outlet
10. Decarburization Chamber
11. Specimen Support Rods
12. Furnace Shell.

end, a differentially wound vertical type electric resistance furnace with a fused quartz decarburization chamber was used. The chamber was large enough to permit the bars to be suspended by $\frac{3}{16}$-inch rods, from the top in such a manner as to allow free circulation of gas around each. Details of this furnace may be seen in Fig. 3. A chromel-alumel thermocouple connected to a controller served as a means of temperature regulation. Temperatures were read directly by means of a potentiometer circuit. The base metal couples were calibrated at intervals against a standard rare metal couple. The moist hydrogen was run in at the top of the furnace, instead of at the bottom, to minimize channeling as much as possible.

Experimental runs were made over a period of fifty hours with saturated hydrogen. The fifty-hour time interval and the saturated hydrogen were used on the basis that the longer duration of time and the very active decarburizing agent (Jominy (2)) would produce results lending themselves more readily to comparisons than those which would be obtained with shorter times and a less active decarburizing medium. Tests were made at temperatures ranging from 1750 down to 1265 degrees Fahr. (955-685 degrees Cent.). The temperatures to which particular attention was paid, however, was the upper and lower hardening limits, and 1300 degrees Fahr. (710 degrees Cent.).

The polished samples were placed in the decarburization chamber, the cap bolted down to insure air-tightness, and the furnace flushed with dry hydrogen before heating up. All samples were allowed to soak for one hour at the decarburization temperature before the electrolytic cell was set in operation. The runs were carried out with a hydrogen flow of six liters per hour, maintaining a back-pressure of about three inches of water in the chamber. After the desired time interval had elapsed, the specimens were permitted to cool in the furnace, the moist hydrogen flow being continued throughout the cooling period. Metallographic sections and turnings for carbon analyses were then taken from the bars.

Carbon determinations were made by combustion in oxygen and a subsequent weighing of the carbon dioxide formed.

It may be stated that due to the uniformity of temperature and gas circulation, and the absence of scaling, decarburization proceeded uniformly over the entire length of each sample. It is to this fact that the unusually constant carbon content of the ferrite band is largely attributed.

The gaseous products of decarburization were analyzed by the absorption method. The absorbents employed for carbon dioxide, unsaturates, oxygen and carbon monoxide were: aqueous potassium hydroxide solution, bromine water, alkaline pyrogallate and cuprous sulphate-beta naphthol solution. The per cent methane was obtained by combustion in a slow-burning pipette containing oxygen, followed by absorption of the carbon dioxide formed in caustic potash solution. Nitrogen analyses were not made.

Results

The object of the first series of tests was to investigate quanti-

Table II
Thermal Critical Points of Steels Investigated

Steel No.	Temperature Degrees Fahr. Ac_1	Temperature Degrees Fahr. $Ac_{3,\,2}$	Steel No.	Temperature Degrees Fahr. $Ac_{3,\,2,\,1}$	Temperature Degrees Fahr. Acm
1	1334	1404	7	1357	1420
2	1341	1405	8	1348	1407
3	1350	1407	9	1342	1416
4	1341	1413	10	1346	1420
5	1348	1413	11	1348	1422
6	1348	1405	12	1359	1436

tatively the influence of grain-size in the surface decarburization of steel.

Specimens were subjected to heats of fifty hours duration at

Table III
Carbon Analyses of Peripheral Turning Taken from Steels No. 1, 2, and 3 Decarburized for 50 Hours at 1450 Degrees Fahr.

Location of Sample	Steel No. 1 Per Cent Carbon	Steel No. 2 Per Cent Carbon	Steel No. 3 Per Cent Carbon
3 Mil Cuts			
1st	0.03	0.03	0.02
2nd	0.02	0.02	0.02
3rd	0.02	0.02	0.02
4th	0.02	0.02	0.02
5th	0.02	0.02	0.02
6th	0.02	0.02	0.02
7th	0.02	0.02	0.04
8th	0.02	0.02	0.08
9th	0.02	0.04	0.14
10th	0.03	0.11	0.21
10 Mil Cuts			
1st	0.24	0.37	0.44
2nd	0.43	0.53	0.58
3rd	0.55	0.62	0.66
4th	0.61	0.68	0.70
5th	0.66	0.71	0.73
6th	0.68	0.73	0.75
7th	0.70	0.75	0.76
8th	0.71	0.76	0.77
9th	0.71	0.77	0.76
10th	0.72	0.76	0.76
11th	0.71	0.77	0.77

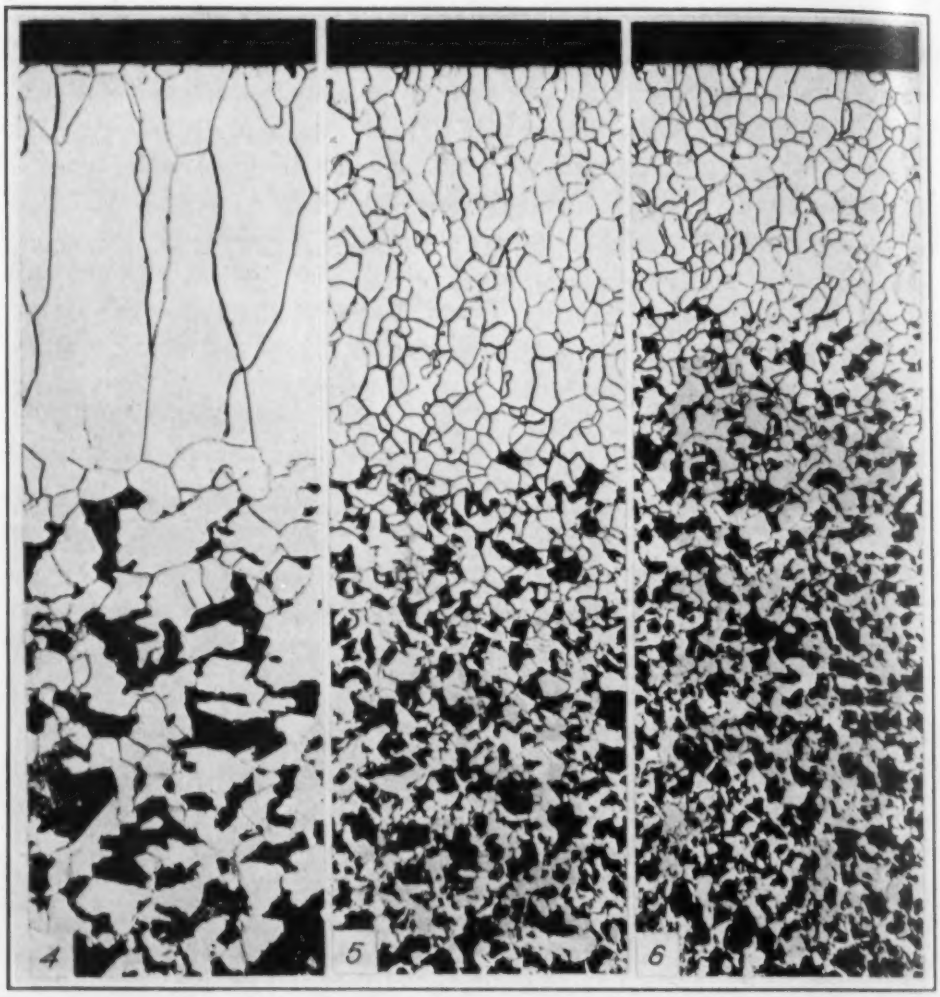


Fig. 4—Steel No. 1 Decarburized for 50 Hours at 1550 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 5—Steel No. 2 Decarburized for 50 Hours at 1550 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 6—Steel No. 3 Decarburized for 50 Hours at 1550 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.

temperatures corresponding to the upper and lower hardening limits, depending upon the carbon content, and at 1300 degrees Fahr. (705 degrees Cent.). Hydrogen saturated with water vapor at room temperature was used as the decarburizing agent. The thermal critical points of steels Nos. 1 to 12 are given in Table II.

Metallographic sections were taken, and carbon determinations made on the above samples at the conclusion of every run. Figs. 4 to 12 illustrate the structure obtained for steels Nos. 1, 2 and 3. The carbon analyses of successive peripheral turnings taken from

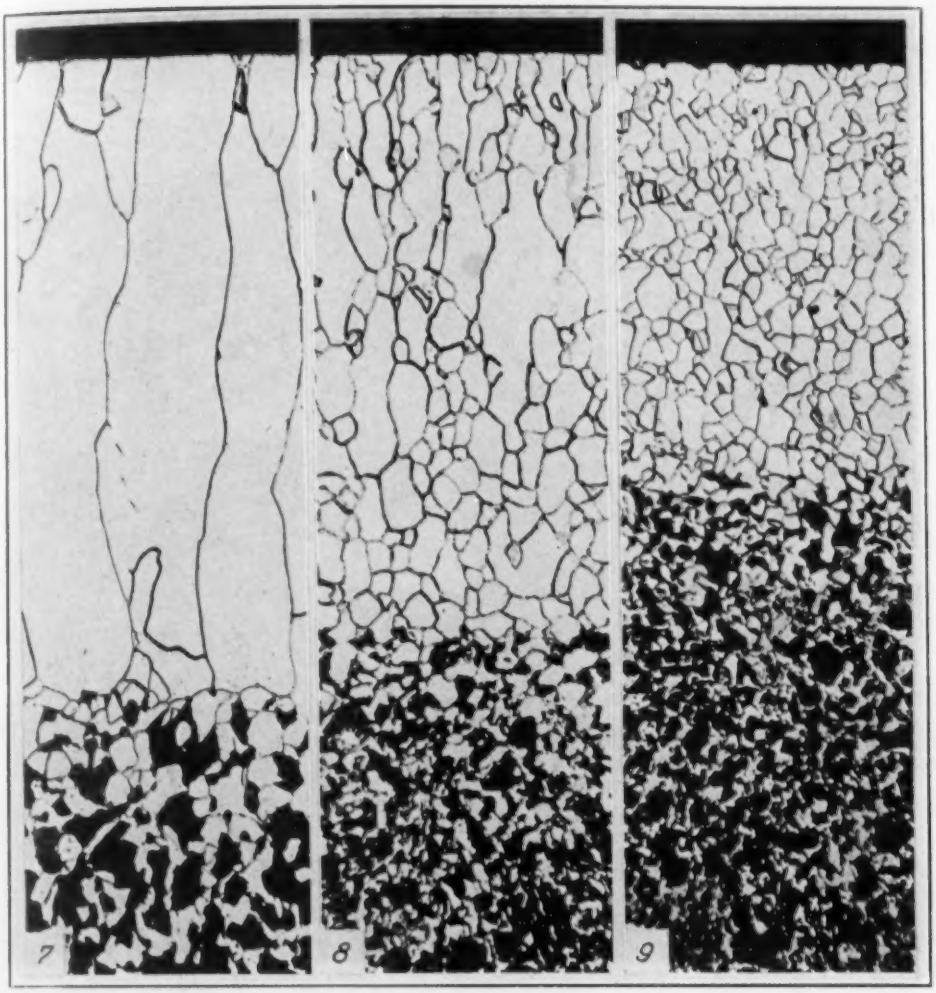


Fig. 7—Steel No. 1 Decarburized for 50 Hours at 1450 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 8—Steel No. 2 Decarburized for 50 Hours at 1450 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 9—Steel No. 3 Decarburized for 50 Hours at 1450 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.

these steels decarburized at 1450 degrees Fahr. (790 degrees Cent.) are recorded in Table III. This data plotted with the mean carbon content of each layer as ordinate, and the mean distance of the layer from the surface of the specimen as abcissa, is shown in Fig. 13.

Experimental runs were next made to reveal the effect of both time and temperature upon the production of a ferrite band. The steels selected were those numbered 1, 2 and 3. After normalizing, bars 3 inches long and 7/8 inch in diameter were turned down from 1 1/8 inch stock and polished with No. 0 emery cloth. The decarburizing

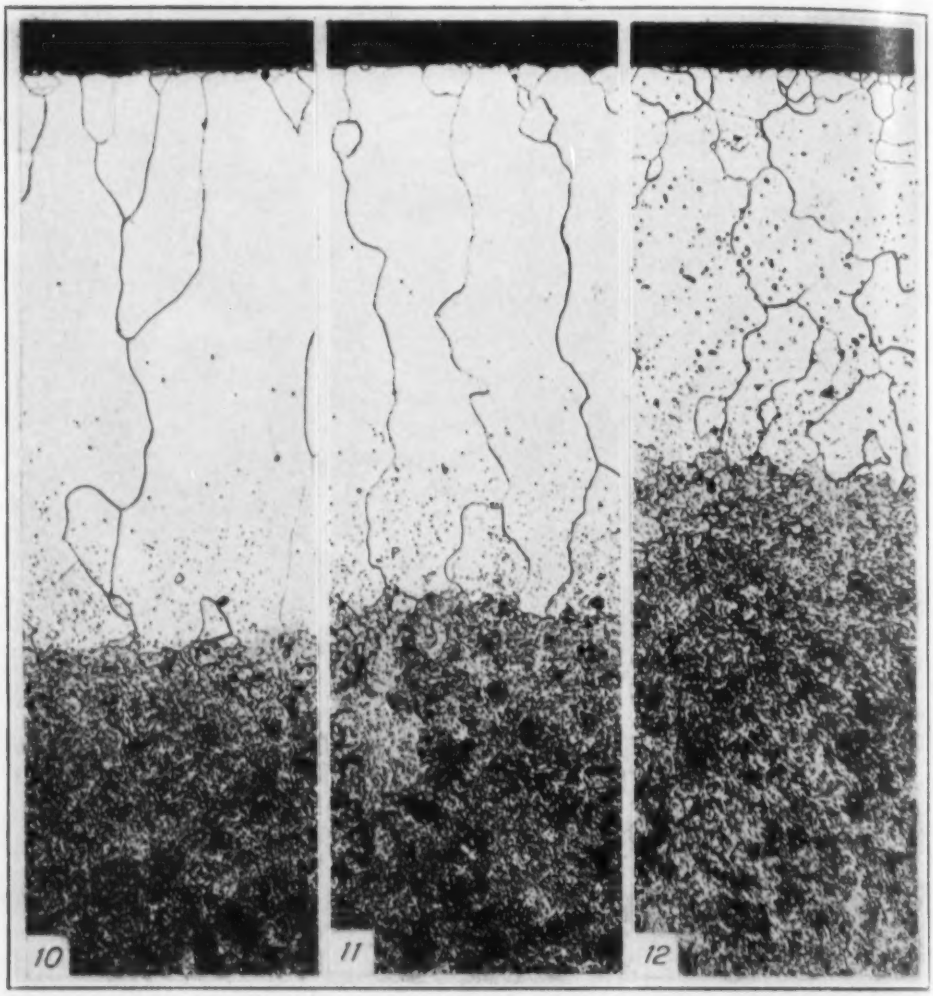


Fig. 10—Steel No. 1 Decarburized for 50 Hours at 1300 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 11—Steel No. 2 Decarburized for 50 Hours at 1300 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 12—Steel No. 3 Decarburized for 50 Hours at 1300 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.

atmosphere was, as before, hydrogen, saturated with water vapor at room temperature.

The method of measuring the width of the ferrite band was by means of a microscope with a micrometer eyepiece. Measurements made by this means upon samples from which turnings had been taken, checked well with the results shown by carbon analyses. An average of several readings on each specimen was accepted as the correct value. To prevent rounding of the edges of sections during polishing, they were mounted in Bakelite.

The effect of time was shown by heating, carried out over time intervals of 5, 10, 15, 20, 25 and 50 hours at a constant temperature of 1350 degrees Fahr. (730 degrees Cent.). The results are given

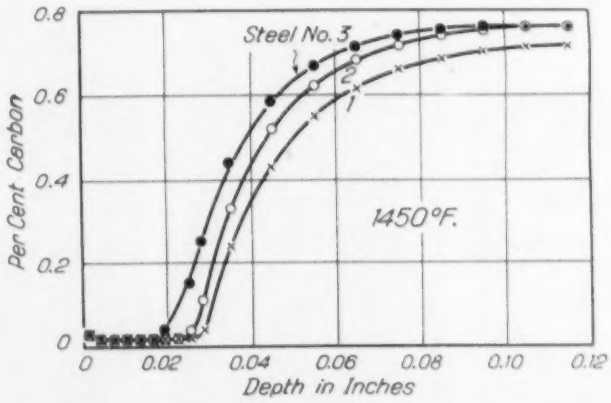


Fig. 13—Carbon Analyses of Peripheral Turnings Taken from Steels Nos. 1, 2 and 3 Decarburized for 50 Hours at 1450 Degrees Fahr.

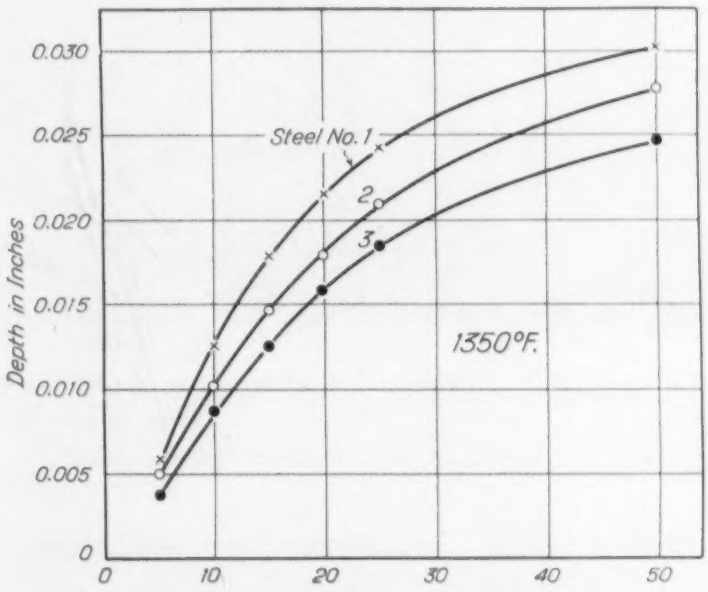


Fig. 14—Relation of the Width of the Ferrite Band to Time at 1350 Degrees Fahr. for Steels Nos. 1, 2, 3.

in Table IV, and in Fig. 14. Photomicrographs of samples decarburized 5, 20, and 50 hours are presented in Figs. 15 to 23.

The variation in the width of the ferrite band with temperature was indicated by heats of fifty hours duration at 1265, 1300, 1350, 1450, 1550, 1625, and 1750 degrees Fahr. (685, 705, 735, 790, 845,

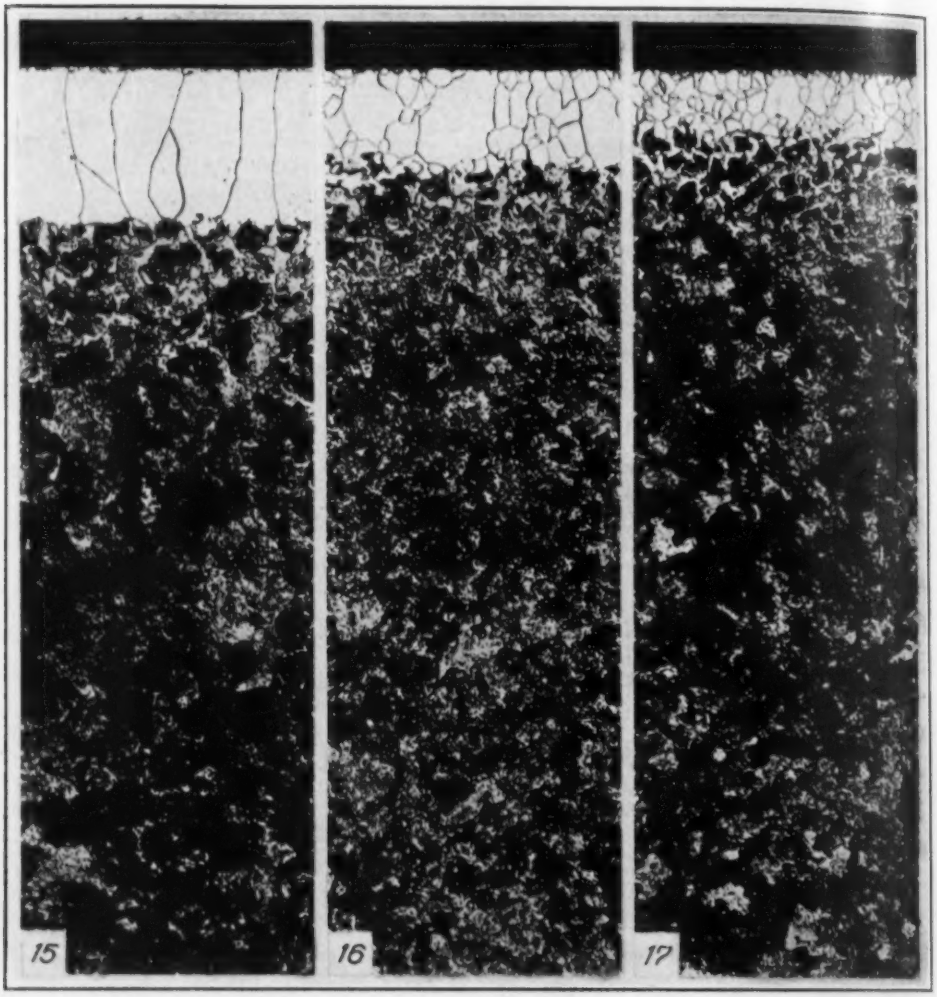


Fig. 15—Steel No. 1 Decarburized for 5 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 16—Steel No. 2 Decarburized for 5 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 17—Steel No. 3 Decarburized for 5 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.

885, 955 degrees Cent.). The microscope readings are shown in Table V, and diagrammatically depicted in Fig. 24.

Table IV
Width of Ferrite Bands for Varying Periods of Time at 1350 Degrees Fahr.

Steel No.	Width in Inches					
	5 Hours	10 Hours	15 Hours	20 Hours	25 Hours	50 Hours
1	0.0059	0.0125	0.0179	0.0214	0.0242	0.0302
2	0.0052	0.0102	0.0146	0.0179	0.0210	0.0278
3	0.0037	0.0087	0.0126	0.0157	0.0185	0.0248

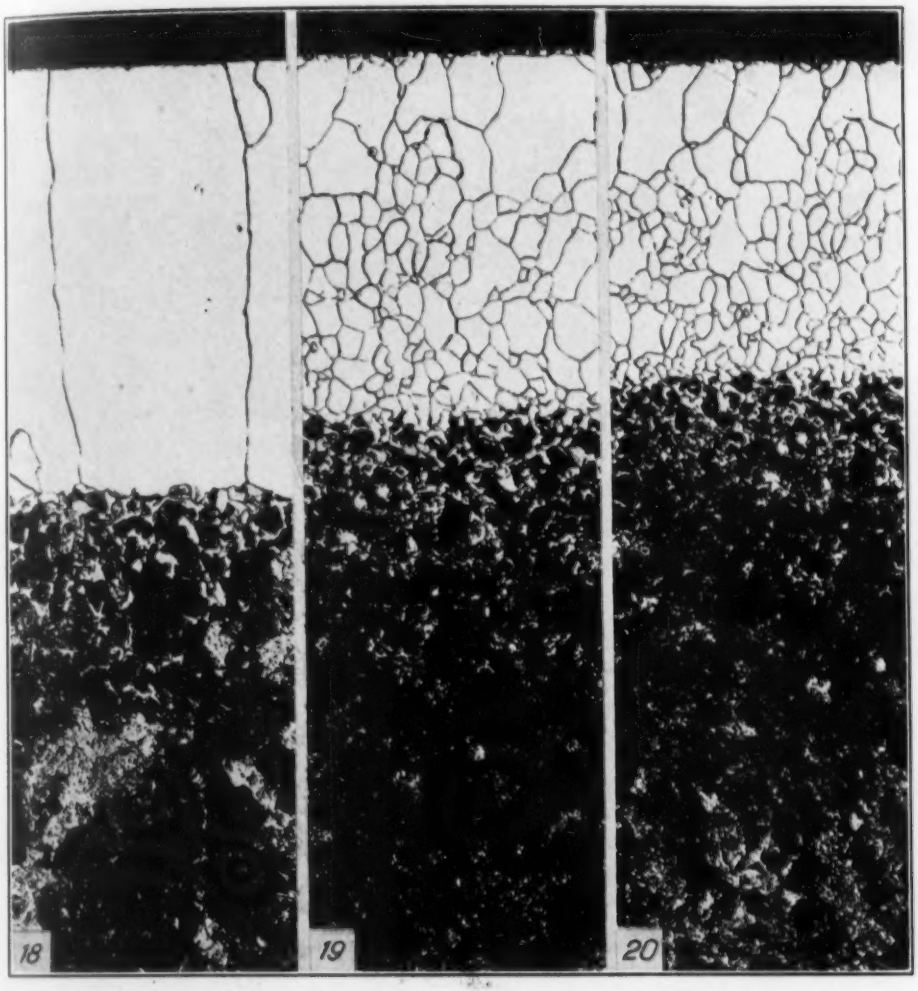


Fig. 18—Steel No. 1 Decarburized for 20 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 19—Steel No. 2 Decarburized for 20 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 20—Steel No. 3 Decarburized for 20 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.

A knowledge of what gases were evolved during decarburization, and in what proportions, seemed indispensable to the formula-

Table V
Width of Ferrite Bands for 50 Hour Decarburizations at Varying Temperatures

Steel No.	Width in Inches						
	1265°F.	1300°F.	1350°F.	1450°F.	1550°F.	1625°F.	1750°F.
1	0.0199	0.0271	0.0301	0.0300	0.0201	0.0155	0.0135
2	0.0169	0.0261	0.0287	0.0278	0.0198	0.0148	0.0130
3	0.0106	0.0185	0.0250	0.0233	0.0138	0.0106	0.0098

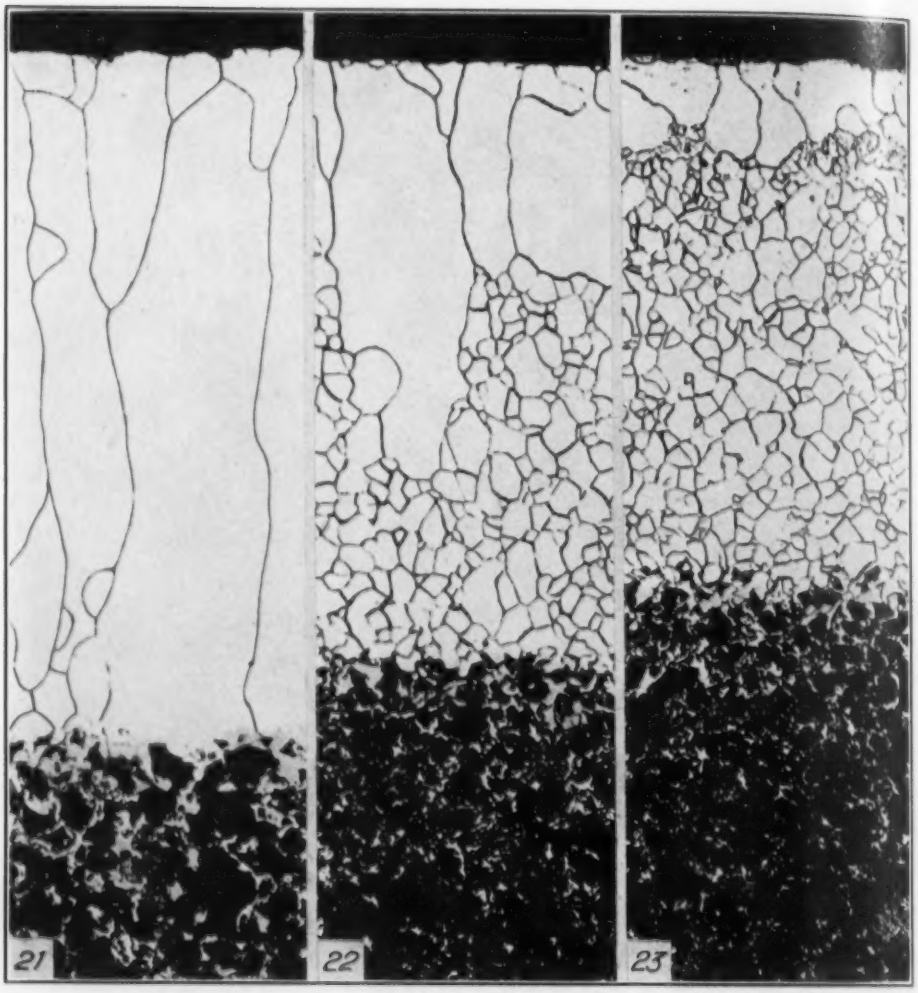


Fig. 21—Steel No. 1 Decarburized for 50 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 22—Steel No. 2 Decarburized for 50 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.
Fig. 23—Steel No. 3 Decarburized for 50 Hours at 1350 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.

tion of a theory for the mechanism of decarburization. Accordingly, gas analyses were made over fifty hour periods at 1300, 1450, and 1700 degrees Fahr. The hydrogen flow was maintained at four liters per hour, and the water concentration was such as to saturate this volume at room temperature. The object in decreasing the volume of hydrogen from six to four liters was to prevent excessive dilution of the carbonaceous gases given off. The steels employed were Nos. 1 and 3. After normalizing, specimens 6 inches long were turned down to a diameter of 1 inch, and pol-

ished. To obtain volumes, of exit gases, commensurate with a reasonable degree of accuracy in analysis, three samples were run simultaneously. This gave a surface area at the start of decarburization of 61 square inches. Analyses were made hourly for the first 10 hours and, thereafter, every 5 hours. The resulting data when plotted, gave the curves of Figs. 25 and 26. None of the determinations showed any carbon dioxide, oxygen or unsaturates.

Columnar Crystals

The formation of columnar crystals in the carbon-free periphery of steel specimens which have been exposed to decarburizing conditions, has been the subject of much discussion by various investigators.

Austin (3) tentatively put forward a theory based on the principle of osmotic pressure. The suggestion was made that the radial pas-

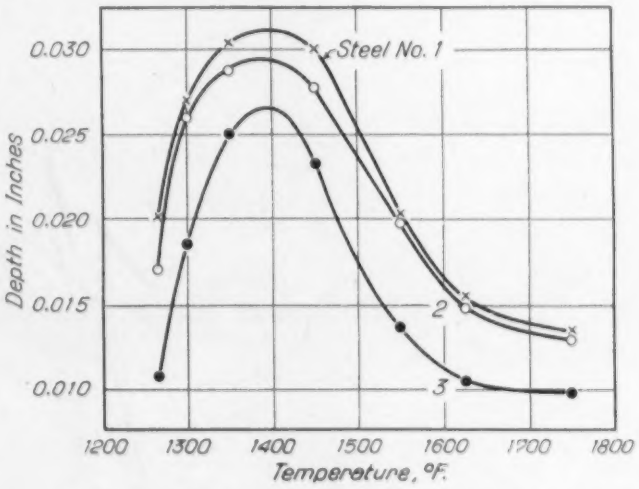


Fig. 24—Effect of Temperature on Width of Ferrite Band. Steels Nos. 1, 2, 3.

sage of hydrocarbon molecules out of the steel produces forces which are assumed to overcome, to some extent, the normal forces of crystallization, thus bringing about a radial or columnar growth within certain temperature ranges.

In order to test this point, two flat samples of No. 10 steel which had been decarburized for 20 hours, and which exhibited a columnar ferrite band 0.0179 inch wide, similar to that of Fig. 18, were subjected to the following treatments: One was cold-hammered until the ferrite annulus had been reduced to less than one-half of its

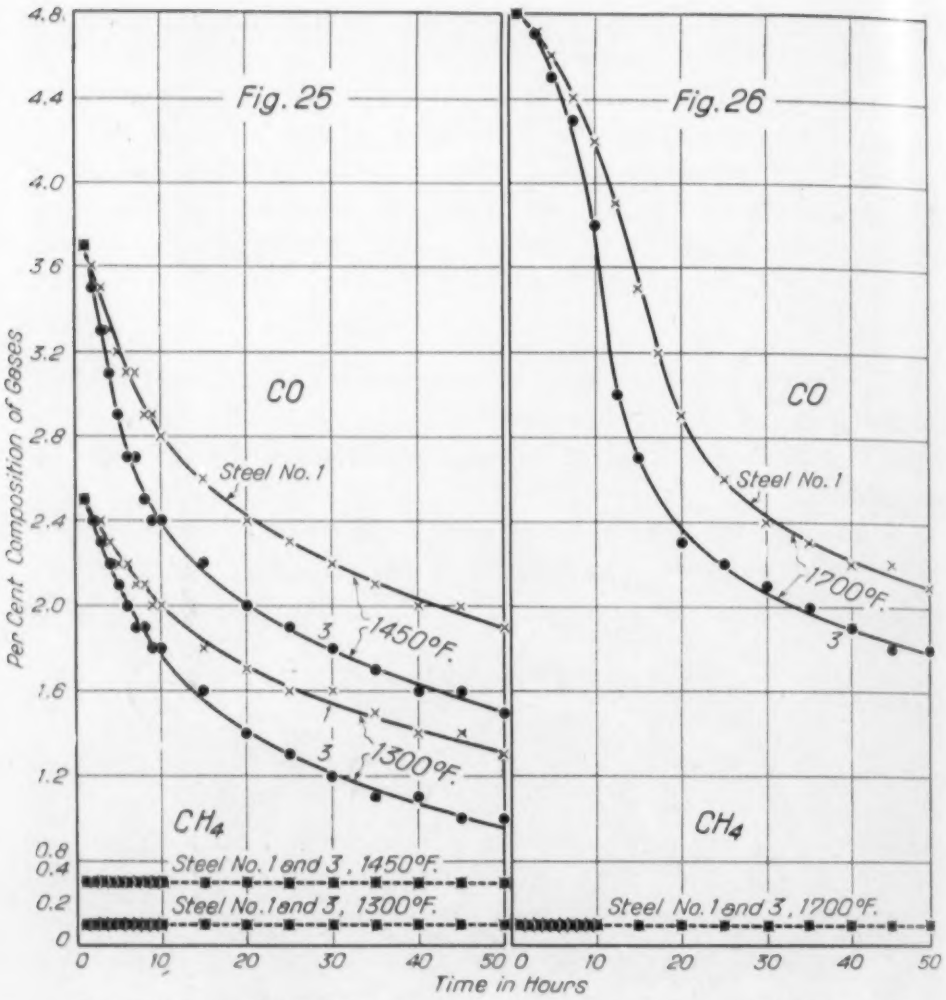


Fig. 25—Composition of the Products of Decarburization as a Function of Time at 1300 and 1450 Degrees Fahr.
Fig. 26—Composition of the Products of Decarburization as a Function of Time at 1700 Degrees Fahr.

original width. After the uneven surface had been leveled by grinding, the specimen was heated to 1350 degrees Fahr. (730 degrees Cent.) to cause recrystallization and grain growth of the ferrite. Fig. 27 shows the radial grains to have been completely destroyed and that in their place a fine-grained polyhedral structure existed. The surface of the re-crystallized specimen was next polished with No. 0 emery cloth and further decarburized at 1350 degrees Fahr. (730 degrees Cent.) in saturated hydrogen for a period of 10 hours. The result is revealed in Fig. 28. The second sample was not cold-hammered but was heated rapidly to a temperature of 1675 degrees Fahr. (910 degrees Cent.). This was accomplished by placing the

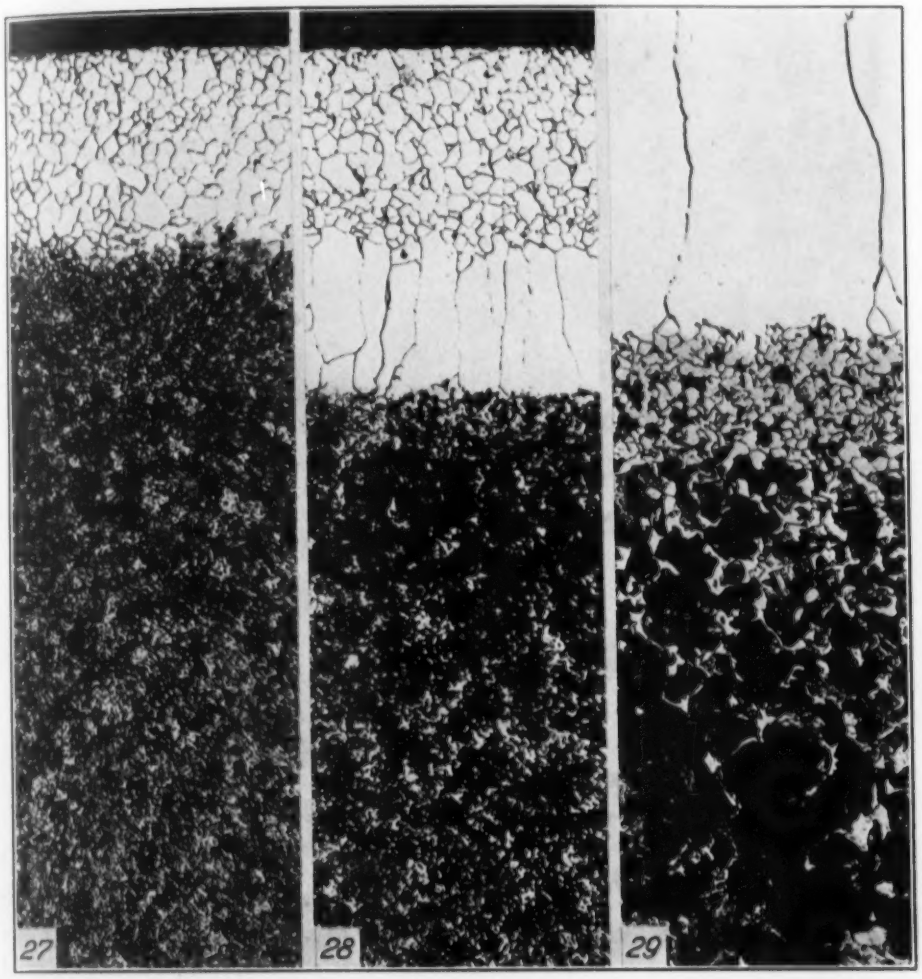


Fig. 27—Structure of Ferrite Band After Cold Working and Recrystallization. × 100.

Fig. 28—Result of Decarburizing Specimen of Fig. 18 for an Additional Period of 10 Hours. × 100.

Fig. 29—Specimen Decarburized for 25 Hours at 1350 Degrees Fahr. and Air-cooled. × 100.

specimen in a furnace already operating at 1675 degrees Fahr. (915 degrees Cent.). When the sample had reached the temperature of the furnace, it was removed and allowed to cool in air. A micro-section showed that the radial ferrite crystals had disappeared, as a result of the phase change, and that only polyhedral grains remained. An additional decarburization of 10 hours duration at 1350 degrees Fahr. (730 degrees Cent.), caused columnar grains to form beneath the equiaxed crystals, as was the case with the first specimen.

These tests would appear to indicate that the columnarization

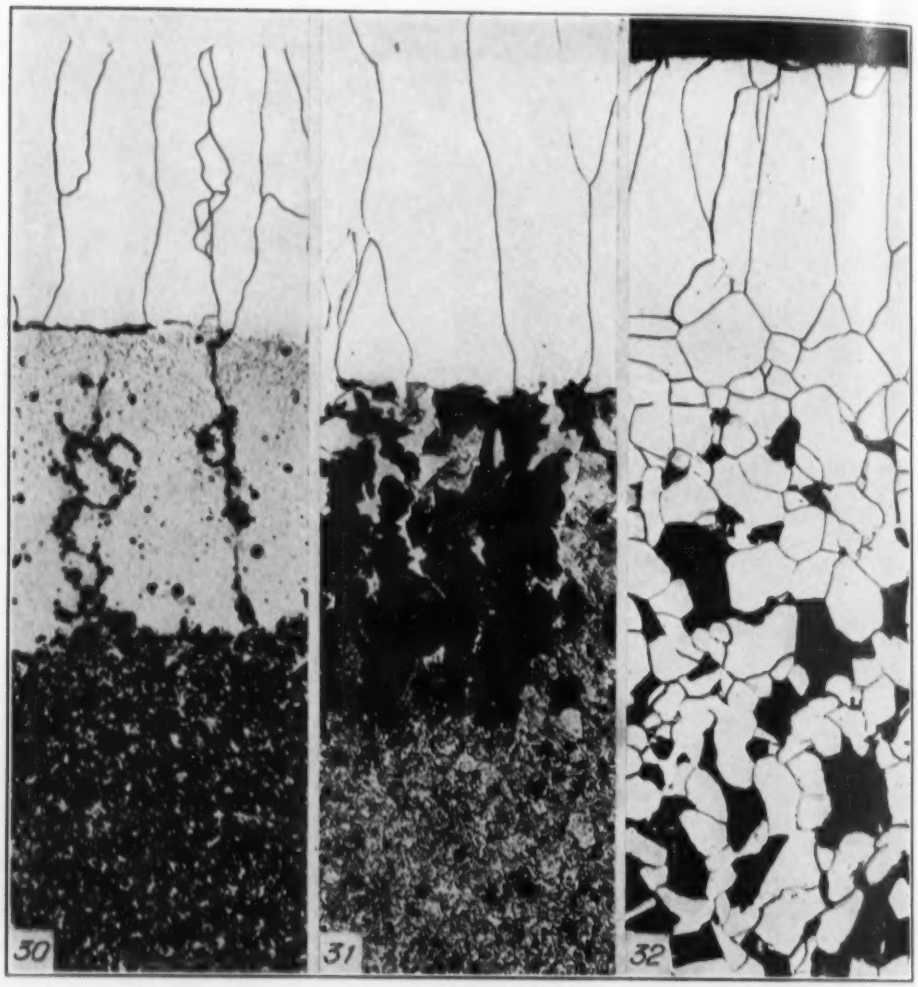


Fig. 30—Specimen Decarburized for 25 Hours at 1410 Degrees Fahr. and Quenched. × 100.
Fig. 31—Specimen Decarburized for 25 Hours at 1410 Degrees Fahr. and Furnace-cooled. × 100.
Fig. 32—Steel No. 1 Decarburized for 50 Hours at 1625 Degrees Fahr. in Hydrogen Saturated with Water Vapor. × 100.

of ferrite, due to decarburization, is not dependent upon the path traversed by gas molecules. It will be seen on comparing Figs. 27 and 28 that there is some extension of the ferrite columns toward the periphery of the section, but this is entirely in accord with the present theory of grain growth.

During the course of this work it was observed that the most pronounced columnarization occurred at temperatures between the Ac_1 and 1450 degrees Fahr. (790 degrees Cent.). On the basis of Austin's theory it might be expected that the higher tempera-

tures, at least up to the A_3 point of pure iron, would be the more favorable to the formation of columnar ferrite, since the steel would be more plastic and greater volumes of gases evolved.

Green (4) points out that when decarburization occurs between 1290 and 1650 degrees Fahr. (700-900 degrees Cent.), "thin zones successively pass through the allotropic transformation from gamma to alpha state, as their composition progressively alters toward the pure iron side of the iron-carbon diagram. Thus arises the peculiar condition of the gamma-alpha change taking place, not with a fall in temperature, but with an alteration of composition at a constant temperature. When the composition first commences to change by loss of carbon, the purer part of the alloy passes through the gamma-alpha change point and grains of the new crystalline alpha phase appear. With the progression of the phase change toward the center of the bar the first formed alpha grains would absorb all of the very much smaller alpha particles which were just recrystallizing from the disappearing gamma modification, providing: (1) that the concentration gradient were steep enough, (2) that the gradient could be maintained; and (3) that the rate of production of the alpha phase actually in process of recrystallization from the allotrope (or the rate of advance of the gamma-alpha change zone) were slower than the velocity of grain growth."

Confirmation of Green's theory was obtained thus: A specimen of No. 1 steel was decarburized for 25 hours at 1350 degrees Fahr. (730 degrees Cent.) in saturated hydrogen. At the end of the run the sample was removed from the furnace and allowed to cool in air from the decarburization temperature. Fig. 29 clearly shows the small alpha grains at the base of the ferrite columns. A second agreement resulted when two samples of No. 9 steel were decarburized simultaneously for 25 hours at 1410 degrees Fahr. (765 degrees Cent.) in saturated hydrogen. After the prescribed time interval had elapsed, one specimen was quenched in water directly from the decarburizing temperature, while the other was permitted to cool down in the furnace. The structure of the quenched section is seen in Fig. 30 and it is apparent that in the area immediately below the ferrite zone, the cooling rate was slightly less than the critical quenching speed. A higher magnification discloses the structure in this region, to be columnar martensite with primary troostite at the column boundaries. Below the radial grains of martensite the structure consists of primary troostite in which is dispersed patches of marten-

site and undissolved spheroids of cementite. Fig. 31 represents the microstructure of the furnace-cooled sample. It is evident that the undissolved spheroids of cementite acted as nuclei for the formation of troostite below the martensite columns in the quenched sample, and, likewise, aids the spheroidization in the same area in the slowly cooled specimen. The above microsections do not show the entire width of the ferrite annulus.

An example in which the velocity of grain growth appears to be less than the rate of the production of the alpha phase is exhibited in Fig. 32. It is hardly to be expected that as steep a carbon concentration gradient could be maintained, under the conditions of the test, as that which would exist at lower temperatures. This conclusion is borne out by comparing the partially decarburized zones of Figs. 21 and 32.

The foregoing tests indicate that, between 1290 degrees Fahr. and 1650 degrees Fahr. (700-900 degrees Cent.), the radial growth of ferrite grains takes place at the expense of small alpha crystals or nuclei formed as a result of the gradual disappearance of the gamma phase; the extent of the growth being dependent upon the steepness of the carbon concentration gradient maintained, and the relative rates of grain growth and decarburization. It is to be understood that these statements do not apply where a steel contains some sort of material which acts to mechanically limit grain growth.

Hultgren (5), Bannister and Jones (6), Kelly (7), and Benedicks (8), appear to hold views similar to that of Green. Hultgren, however, points out "that it does not seem necessary to assume that particles of alpha formed in transformation are immediately absorbed by the previously existing grains, since in that case recrystallization would be involved."

Edwards and Yokoyama (9) have shown that radial ferrite grains could be obtained at temperatures below the A_1 by subjecting to decarburization specimens which had been deformed slightly beyond their elastic limit. These authors are of the opinion that columnarization is due to some kind of a transient stress.

It becomes necessary at this point to account for the ferrite columnarization which occurred to a greater or less degree in all samples decarburized at 1300 degrees Fahr. (705 degrees Cent.) in the present investigation.

With the beginning of decarburization below the A_1 transformation point, a somewhat different condition than that for above the A_1

is set up. Ferrite crystals or nuclei are now formed not as a result of a gamma to alpha phase change, but rather as a consequence of the removal of the carbon from the iron carbide phase. As these minute alpha particles are liberated at successive depths below the surface of the specimen, with the progression of decarburization, conditions highly favorable to radial grain growth exist, providing that the carbon gradient is steep enough.

Initial grain growth may be assumed to take place in either or both of the following ways: (1) the newly formed ferrite particles or nuclei may adopt the orientation of the parent grain, i.e., the orientation of the residual ferrite, and columnar growth take place by boundary extension of this surface grain; or (2) the ferrite particles or nuclei may crystallize and grow by the absorption of the parent grain and the subsequently formed ferrite particles. It is quite probable that transient stresses (Edwards and Yokoyama) are set up as a result of decarburization below the A_1, and these stresses may have an important bearing upon the production of columnar crystals within this temperature range.

On the basis of the above theory, it is to be expected that low carbon steels, when subjected to decarburization at temperatures below the gamma to alpha change point, would show little or no ferrite columnarization because the carbon gradient is not sufficiently steep. The higher carbon steels, on the contrary, would exhibit a more perfect columnarization with increasing carbon content. No low carbon steels were tested in the present work, but it was observed that the radial character of the ferrite zone became decidedly more pronounced as the carbon content of the steels increased from 0.71 to 1.07 per cent.

On the basis of the assumed mechanism of their formation, there is reason for believing that columnar grains, resulting from the decarburization of steel, should show a certain preferred orientation common to the entire band of crystals. It was decided to investigate this possibility by means of X-ray measurements. Considerable work was done in an effort to settle the point but, unfortunately, the results obtained were not decisive due to the difficulty experienced in isolating single crystals. That a preferred orientation does in all probability exist, however, was indicated by a persistent zoning effect which was always present when shots were taken through layers of metal two or more crystals thick.

Table VI

Results of 50 Hour Decarburizing Periods at Upper and Lower Hardening Limits, and at 1300 Degrees Fahr.

Steel No.	1550°F. A	B	C	D	1450°F. A	B	C	D	1300°F. A	B	C	D
1	0.0201	0.1750	0.0388	0.0545	0.0300	0.1050	0.0330	0.0465	0.0271	0.0478	0.0229	0.0323
2	0.0198	0.1325	0.0348	0.0458	0.0278	0.1000	0.0318	0.0413	0.0261	0.0453	0.0210	0.0276
3	0.0138	0.1200	0.0309	0.0407	0.0233	0.0950	0.0279	0.0362	0.0185	0.0418	0.0177	0.0233
4	0.0212	0.1850	0.0428	0.0595	0.0354	0.1200	0.0356	0.0495	0.0331	0.0568	0.0257	0.0357
5	0.0212	0.1400	0.0386	0.0507	0.0299	0.1100	0.0347	0.0456	0.0271	0.0481	0.0225	0.0296
6	0.0126	0.1325	0.0357	0.0470	0.0252	0.1050	0.0312	0.0410	0.0200	0.0448	0.0191	0.0248
	1460°F.				1410°F.				1300°F.			
7	0.0305	0.1140	0.0447	0.0475	0.0315	0.0950	0.0400	0.0425	0.0251	0.0508	0.0286	0.0304
8	0.0186	0.0950	0.0336	0.0362	0.0199	0.0800	0.0310	0.0337	0.0165	0.0418	0.0212	0.0230
9	0.0265	0.0940	0.0450	0.0445	0.0278	0.0750	0.0404	0.0400	0.0239	0.0370	0.0270	0.0268
	1430°F.				1390°F.				1300°F.			
10	0.0287	0.0850	0.0425	0.0425	0.0278	0.0700	0.0384	0.0384	0.0218	0.0448	0.0272	0.0272
11	0.0252	0.0780	0.0409	0.0409	0.0239	0.0650	0.0363	0.0360	0.0218	0.0418	0.0272	0.0268
12	0.0305	0.0800	0.0463	0.0440	0.0292	0.0700	0.0418	0.0398	0.0218	0.0328	0.0236	0.0221

A = Width of ferrite band in inches.
B = Maximum depth of decarburization in inches
C = Degree of decarburization.
D = Degree of decarburization per unit of original carbon content.

Discussion of Results

The maximum depth of decarburization signifies, in a qualitative way only, the degree of decarburization, i.e., the amount of carbon removed from a steel during a decarburization run. In the course of this work, several instances were encountered in which steels of different grain-size and carbon contents showed practically the same depth of decarburization, but differed markedly in the amount of carbon lost. It was for this reason that curves of the type illustrated in Fig. 13 were made. These graphs not only indicate the total depth of decarburization and character of the partially decarburized zone, but the areas under them (Fig. 33) may be used for comparative purposes. Johansson and von Seth (10) employed the same method in determining relative degrees of decarburization.

In order to place experimental results upon a common basis. insofar as carbon is concerned, the calculated area under each curve was divided by the original carbon content of the steel for which the graph was made. The figure obtained in this way represents the degree of decarburization per unit of carbon originally present in the steel.

Table VI gives the decarburization data for the twelve steels tested at their upper and lower hardening limits, and at 1300 degrees

Fahr. (705 degrees Cent.). The one exception was the steel labeled No. 9 which was run at 1410 and 1460 degrees Fahr. (765-795 degrees Cent.). It will be seen that, under the conditions of the tests, the carbon loss for the coarse-grained steels was greater than that for the fine-grained steels. At a given decarburization temperature the grain-size of an inherently fine-grained steel was definitely smaller than that of the coarse-grained steel with which it was

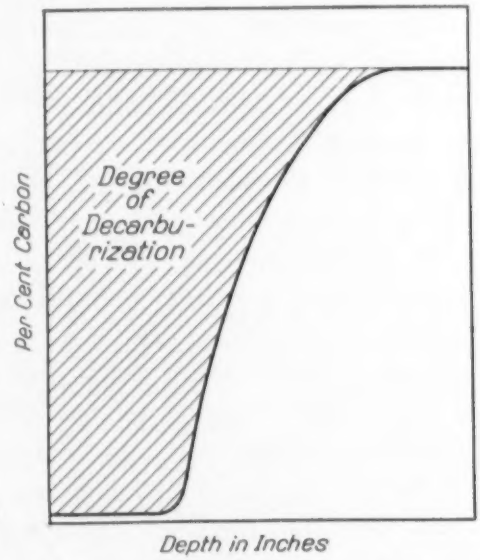


Fig. 33—Graph Illustrating Method of Determining the Degree of Decarburization.

being compared. The increase in grain-size at the upper hardening limit, over that existent at the lower limit, was negligible so far as the relative amounts of carbon lost from a steel at those two temperatures were concerned.

The time runs at 1350 degrees Fahr. (735 degrees Cent.) (Fig. 14) indicate that for both fine and coarse-grained steels the maximum rate of decarburization occurs within the first 25 hours. It is to be noted that the three curves maintain about the same relative positions throughout.

A consideration of Fig. 24 reveals that for the three steels tested, a ferrite band of maximum width occurs at approximately 1400 degrees Fahr. (760 degrees Cent.). This is the temperature at which these steels become entirely austenitic on heating (Table II).

The sharp decline of the curves between 1400 and 1650 degrees Fahr. (760-900 degrees Cent.) is attributed to three factors:

(1) an increased rate of diffusion of carbon toward the peripheral parts of the samples, (2) an acceleration in the activity of the agent causing the removal of carbon; and (3), a larger amount of carbon must be removed, before a ferrite precipitation becomes possible, as the A_3 point of pure iron is approached, due to the slope of the A_3 line of the iron-carbon diagram. Above 1650 degrees Fahr. (900 degrees Cent.) it may be assumed that only the first two factors are in operation, hence the flattening of the curves in this region. That the second factor is the predominating one, however, is evidenced by the fact that a ferrite band of considerable width is formed at a temperature as high as 1750 degrees Fahr. (955 degrees Cent.). It is recognized that furnace cooling from 1750 degrees Fahr. (955 degrees Cent.) will augment the width of the ferrite zone, but the cooling time was less than three hours and could not have accounted for the entire width of the band shown. Further, all runs were made in exactly the same way and the results obtained should serve for purposes of comparison.

As the decarburization temperature drops below 1400 degrees Fahr. (760 degrees Cent.), the ferrite zone narrows rapidly due to the low solubility of carbon in alpha-iron, and because of the decreasing activity of the decarburizing agent at lower temperatures.

Experimental data show that the lower the temperature at which the carbon removal takes place, the sharper will be the line of demarcation between the ferrite annulus and the partially decarburized zone adjacent to it.

Mechanism of Decarburization

Stead (11), Hatfield (12), Würst (13) and Emmons (14) have attributed the removal of carbon from iron-carbon alloys during decarburization to a reaction between carbon or iron carbide and carbon dioxide, the carbon dioxide being partially reduced to carbon monoxide in the process. In the words of Stead, "any" active oxidizing agent such as air, steam, or oxide, capable of readily parting with its oxygen, may be the primary source of oxygen; but it appears that they are only the means by which the carbon dioxide and carbon monoxide are produced, and it is the carbon dioxide which is directly responsible for the oxidation and removal of carbon." It was believed by Stead that with the formation of a ferrite band, it became necessary for the oxidizing gases to diffuse into the metal

and react with the outwardly diffusing carbon at some reaction interface, the carbon being completely oxidized as rapidly as it diffused beyond this clearly defined boundary.

Ledebur (15), as a result of some studies made upon white pig iron, and upon malleable iron rods which had been exposed to highly heated furnace gases, held that in decarburization a migration of oxygen from molecule to molecule from the surface of a specimen to the reaction interface might be inferred without requiring the gases to penetrate into the interior.

Austin (1) gives as the basic chemical reactions involved in surface decarburization of steel by moist hydrogen:

$$(1)\quad Fe_3C + 2H_2 = 3Fe + CH_4$$
$$(2)\quad Fe_3C + O = 3Fe + CO$$

the oxygen originating from the decomposition of the water vapor.

Inasmuch as the analyses of the products of decarburization at the different temperatures showed an absence of carbon dioxide in all cases, it seems highly improbable that carbon dioxide should be the agent responsible for the carbon removal. Austin has already indicated that hydrogen alone has a real but limited decarburizing power. The results of the analyses of the products of decarburization lend confirmation to this viewpoint. The possibility of oxygen as liberated by the decomposition of the water vapor functioning as the active agent remains. Do the conditions present provide for the possible diffusion of oxygen from the outer surface of the specimen to the interface? If so, one would expect the steel after decarburization to show an increased oxygen content. The analysis of steel before decarburization shows 0.0006 per cent. After decarburization, the ferrite band analyzes for steels decarburized at 1450 degrees Fahr. for (790 degrees Cent.) for periods of time up to two months, 0.0025 to 0.0027 per cent oxygen.

It appears probable that the oxidation of carbon is brought about by the transfer of oxygen, in solution in the ferrite. That the reaction between carbon and oxygen takes place at some reaction interface, below the surface of a sample, is evidenced by the relatively sharp line of demarcation between the ferrite band and the adjacent zone.

Assuming solid diffusion to be the means by which most of the oxygen reaches the reaction interface, columnar grains would offer less resistance to this diffusion than would small equiaxed crystals,

because of the limited amount of grain boundary material present in such a crystal structure. It would follow, therefore, that the rate of decarburization would be greater for coarse-grained steels than for fine-grained steels of like chemical composition.

Summary and Conclusions

A study of the influence of grain-size upon the surface decarburization of steel by moist hydrogen revealed that fine- and coarse-grained steels of substantially identical composition do not decarburize to a like degree. When subjected to the same decarburizing conditions, the coarse-grained steels undergo the greater loss of carbon.

The effects of time and temperature on the character and width of the totally decarburized zone for fine- and coarse-grained steels was determined. The relative widths of the ferrite bands of coarse- and fine-grained steels remained practically independent of the time at the decarburization temperature. The maximum width of the ferrite band of both fine- and coarse-grained steels was found when decarburization occurred at approximately the A_3 transformation point of the steels investigated.

Consideration was given to the structure of the ferrite band as formed above and below the A_1 point. Data was submitted in support of the previously advanced theory that ferrite columnarization between 1290 and 1650 degrees Fahr. (700-900 degrees Cent.) takes place as a result of the gamma to alpha phase change.

A theory was put forward to explain the mechanism of ferrite columnarization below the A_1 point.

Analyses of the gaseous products of decarburization were made, and an explanation of the mechanism of decarburization advanced.

Acknowledgments

The authors desire to express their indebtedness to the Carnegie Steel Company, Pittsburgh, for the contribution of the steels which have made these investigations possible; to Dr. John Chipman for many helpful hints in improving experimental technique; to Dr. L. Thomassen for assistance in X-ray crystal analysis; and to Dr. L. O. Case for counsel concerning the probable mechanism of decarburization.

Bibliography

1. C. R. Austin, "Effect of Water Vapor on the Surface Decarburization of Steel by Hydrogen," TRANSACTIONS, American Society for Metals, Vol. XXII, 1934, p. 31.
2. W. E. Jominy, "The Surface Decarburization of Steel at Heat-Treating Temperatures," University of Michigan Research Bulletin, No. 18, 1931.
3. C. R. Austin, "Hydrogen Decarburization of Carbon Steels with Considerations on Related Phenomena," *Journal*, Iron and Steel Institute, Vol. I, 1922, p. 93.
4. G. W. Green, Discussion of Austin's paper: "Hydrogen Decarburization of Carbon Steels with Considerations on Related Phenomena," *Journal*, Iron and Steel Institute, Vol. I, 1922, p. 147.
5. A. Hultgren, Discussion of Kelley's paper: "Grain Growth in Metals Caused by Diffusion," *Transactions*, American Institute of Mining and Metallurgical Engineers, Institute.
6. C. O. Bannister and W. D. Jones, "The Diffusion of Tin into Iron with Special Reference to the Formation of Columnar Crystals," *Journal*, Iron and Steel Institute, Vol. II, 1931, p. 71.
7. F. C. Kelley, "Grain Growth in Metals Caused by Diffusion," *Proceedings*, American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, 1928, p. 390.
8. C. Benedicks, Discussion of Kelley's paper: "Grain Growth in Metals Caused by Diffusion," *Proceedings*, American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, 1928, p. 402.
9. C. A. Edwards, and T. Yokoyama, "The Influence of Varying Strains and Annealing Temperatures on the Growth of Ferrite Crystals in Mild Steels," 1928, Vol. II, p. 141.
10. A. Johansson and R. von Seth, "The Carburization and Decarburization of Iron and Some Investigations on the Surface Decarburization of Steel," *Journal*, Iron and Steel Institute, Vol. II, 1926, p. 295.
11. J. E. Stead, "The Crystalline Structure of Iron and Steel," *Journal*, Iron and Steel Institute, Vol. 53, 1898, p. 145.
12. W. H. Hatfield, "The Chemical Physics Involved in the Decarburization of Iron-Carbon Alloys," *Journal*, Iron and Steel Institute, Vol. 1, 1909, p. 242.
13. F. Wüst, "The Theory of Malleabilization," *Metallurgie*, Vol. 5, 1908, No. 1, p. 11.
14. J. V. Emmons, "Surface Decarburization of Tool Steel," *Journal*, American Institute of Mining and Metallurgical Engineers, Vol. 50, 1914, p. 405.
15. A. Ledebur, Discussion of Stead's paper: "The Crystalline Structure of Iron and Steel," *Journal*, Iron and Steel Institute, Vol. 53, 1898, p. 199.

DISCUSSION

Written Discussion: By C. R. Austin, Assistant Professor, Department of Metallurgy, Penn State College, State College, Pa.

I am very pleased to have the opportunity to discuss this paper on surface decarburization of steel. If I may digress for a moment, it was about 15 years ago that the general subject of decarburization provided me with one of my first subjects for research in the laboratory of Professor C. A. Edwards in Manchester. Professor Edwards was interested in the use of electrical con-

ductivity measurements as a correlative means of elucidating the constitution of chromium steels. In order to eliminate the effect of carbon and permit a more definite evaluation of the role played by chromium, manganese and silicon I attempted to completely decarburize the alloys, in the form of 1-centimeter diameter bars, in moist hydrogen at 1000 degrees Cent. (1830 degrees Fahr.). The rate of carbon elimination was so slow that the work was abandoned. However, the interest stimulated by the work resulted in the research published in 1922. Data on the effect of chromium were submitted as a contribution to a research by Campbell, Ross and Fink in 1923. In a recent paper cited by the authors further evidence of the stabilizing effect of chromium additions on the carbide is also presented.

At that period the interest in gas-metal reactions was not nearly so general nor was it considered so important as today, although an immediate application of the results of this work was found in the well-known research of Edwards and Pfeil who produced the first single crystal test samples of pure iron. These workers failed in their objective when attempting to apply critical stress to Armco iron but were completely successful when similar experimental technique was applied to hydrogen decarburized mild steel.

So far as I am aware the present paper represents the first research conducted to determine the role of grain-size on decarburization and I am very pleased to note the thorough manner in which the authors have attempted to obtain conclusive data on this phase of the subject. Possibly they were unwise in assuming that nitrogen was not of sufficient importance to warrant removal and I would suggest that the addition of the phosphorus pentoxide was unnecessary.

The general method of gas purification as stated in the paper is very similar to one I outlined before this Society two years ago and I am particularly interested in their reference to stainless steel as an indicator of gas purity. I should like to ask the authors to give us some information regarding the behavior of this testing method more particularly with reference to the facility with which they prepared pure gas. It seems a little surprising that no metallic reducing agent such as chromium was necessary in the purification train. Nitrogen in quantity will undoubtedly tarnish stainless steel but perhaps in the authors' experiments the concentration was too low to exhibit this effect within the test time employed.

It is to be noted that three specimens were run simultaneously. Presumably it is safe to assume that they were all of like carbon content since otherwise the interpretation of data is uncertain.

At this point I should like to record that this paper appears to infer, and other recent references to my work on the subject similarly assume, that I have stated that hydrogen had a negligible decarburizing power at any elevated temperature. It should be emphasized that the study of the effect of water vapor related specifically to 800 degrees Cent. (1470 degrees Fahr.). It is unwise to assume that similar conditions obtain at other temperatures.

The general results on surface decarburization are beautifully depicted in the series of photomicrographs which in the opinion of the writer are remarkable for their detail. Confirmation of these structures is provided in the analytical data from peripheral trimmings.

An important contribution of the authors is in the use of gas analysis for the products of reaction and their results are condensed in Figs. 25 and 26. It is necessary to study these diagrams for a little while before it becomes apparent that the methane concentration remains constant with increase in time of experimentation in contrast to the decrease in concentration of carbon monoxide.

The authors' data on oxygen concentration in the peripheral ferrite and their inference on the mechanism of decarburization is of particular importance. In my own work I believe I effectively demonstrated that pure hydrogen may result in decarburization but this referred specifically to reactions at the gas-metal interface. In the presence of water vapor a zone of uniformly low carbon content (as obtained by the present authors) was revealed and it was suggested that since this condition did not permit simply the conception of a concentration gradient from cone to periphery it was necessary to postulate gaseous diffusion leading to decarburization within the surface of the steel. Many metallurgists apparently find it difficult to accept this view. The increase in oxygen concentration of the steel during decarburization discussed on page 123, gives further credence to this theory, however, and it appears likely that oxygen penetration resulting from peripheral oxidation of the iron leads to oxygen diffusion toward the core with formation of carbon monoxide actually below the surface of the metal. Evidently the carbon monoxide diffuses back towards the surface and thus leaves the metal at the interface.

Again referring to Figs. 25 and 26 it is interesting to examine the possible significance of the fact that the concentration of methane is constant throughout the tests, while that of the carbon monoxide progressively decreases. Does this suggest that:

(1) The hydrogen reaction takes place alone at the gas-metal interface and that the carbon concentration at this boundary is always sufficiently high to maintain a uniform rate of reaction?

(2) The monoxide reaction is at least partially a solid solution reaction, and as the peripheral parts are denuded with respect to carbon the oxidation by progressive diffusion penetration into the metal introduces a time factor which results in slowing down the rate of CO formation?

The shape of the curves in Fig. 26 are particularly in accord with this view.

In my opinion there appears little reason to anticipate the presence of carbon dioxide in quantity in the effluent gases.

Comments might well be made on the theory of the formation of columnar crystals concomitant with decarburization and on the effect of grain-size but I will conclude by congratulating the authors on their real and important contribution to our knowledge of the subject of surface decarburization of steels.

Written Discussion: By W. E. Jominy, General Motors Co., Detroit.

The authors have given us an excellent paper and deserve congratulations. They have chosen an experimental method which permits the highest accuracy of results and I am particularly impressed with their method of adding measured amounts of water vapor to the hydrogen. Water vapor is a very active

decarburizer when present in small percentages not only in the presence of hydrogen but also nitrogen. Oddly enough when large percentages of water vapor are present or with 100 per cent of water vapor, decarburization proceeds at a much slower rate. This is probably due to the formation of scale on the steel surface which sets up an interference to the diffusion of gas into the steel. Furthermore, some of the metal which would have been decarburized iron is changed into iron oxide. Any condition under which water vapor or oxygen can come in contact with steel without forming scale will be found to give faster decarburization than when scale is formed.

We ordinarily think of decarburization as a phenomenon to be avoided in the fabrication and hardening of steel. There are, however, a few instances where decarburization is desired and one is able to see commercial possibilities if an easy means of decarburization were possible. So far as the writer knows, moist hydrogen is the fastest decarburizing agent available. Have the authors any knowledge of any medium which might be faster or more convenient than this gas? A research in this direction would be of considerable practical importance.

The authors' account of the mechanism of decarburization as being accomplished in part by the diffusion of oxygen into the metal to the reaction interface seems entirely satisfactory. Probably the reason for moist hydrogen being so active a decarburizer is due to the ease of diffusion of atomic oxygen which is liberated at the steel surface and to the absence of scale. It is easy to conceive of atomic oxygen diffusing in, but more difficult to conceive of molecular carbon monoxide diffusing back out. It is, of course, quite as necessary for the carbon monoxide to get out as for the oxygen to get in.

The decarburization below A_1 gives added evidence that the mechanism of decarburization consists of the penetration of gas, since the very slight solubility of carbon in alpha iron makes it impossible to account for the decarburization on the basis of the migration of carbon in the iron.

The writer has produced decarburization with moist hydrogen at temperatures as low as 1000 degrees Fahr. and has found with these lower temperatures a very sharp line of demarcation between the ferrite and partially decarburized zone adjacent to it, which is in agreement with the report of the authors.

There seems to be a tendency for the fine-grained steels to form columnar crystals only at the surface of the sample as shown in Figs. 19, 20, 22 and 23. While it is probably true that these crystals were the first formed and, consequently, have had more time to absorb the smaller crystals, the fact that they seem to start only at the surface may be of some significance. The authors have not mentioned this phenomenon. Do they have an explanation for it?

Oral Discussion

J. Q. Adams:[1] It might be of interest to the authors to know there has been developed a meter capable of measuring moisture in hydrogen to the extent of better than one-tenth of 1 per cent of water by weight of hydrogen.

[1]General Electric Co., Schenectady, N. Y.

We do not know the limits of this apparatus but we do believe it is accurate to one-tenth of 1 per cent.

T. D. YENSEN:[2] I regret that I did not have an opportunity to study this paper very carefully. I have just a few short remarks to make. In accordance with the evidence that we have obtained at the Westinghouse Laboratories it seems that the combination between carbon and oxygen takes place on the surface, in other words, that carbon diffuses from the interior to the surface where it combines with the oxygen and escapes as CO. I would like to have some further comments by the authors of the paper in regard to this point because it certainly is a very interesting one.

H. J. FRENCH:[3] In looking over the paper I have a little difficulty in determining just what the authors believe the sequence of events to be and personally I would like to have Mr. Rowland elaborate a little on this point if he will. In view of the prior discussion, it might be interesting also to have some further comments covering the reasons why coarse-grained steel seems to decarburize more rapidly than fine-grained steels.

C. E. SIMS:[4] The contentions of the authors that the fine-grained steel decarburizes slower than the coarse-grained steel is very well substantiated by their data and discussion. This seems to be a rather logical outcome. If we think of decarburization as a matter of diffusion, it seems to follow quite naturally that the fine-grained steel should decarburize slower than the coarse-grained steel. Apparently, the reason fine-grained steels are fine-grained, is because of some sort of mechanical interference with the diffusion of the constituents.

As to the place of the reaction between carbon and oxygen, which is the principal cause of decarburization, it seems to me very difficult to conceive of its taking place below the metal surface. We know that carbon atoms diffuse very readily in gamma iron, and much less readily in alpha iron. Atomic hydrogen diffuses very readily in iron, and oxygen less readily, but the diffusion of molecular CO seems to be almost ruled out in the rate of decarburization that is obtained. A subsurface reaction would necessitate a complex counter current diffusion of oxygen and CO. Evidence that seems to contradict this theory was mentioned in Mr. Jominy's discussion. He showed that when we have a heavy scale or a highly oxidizing condition, we do not get as rapid decarburization. It will be noticed on the pictures shown here that with a moist hydrogen there was practically no evidence of iron oxide in the surface ferrite. When you have a highly oxidizing condition and a heavy scale there are iron oxide inclusions in the ferrite grains near the surface: evidence that there is actually more oxygen in the steel. Under such conditions one would expect more rapid decarburization instead of less. It seems more likely that decarburization occurs by diffusion of the carbon to the surface, where it reacts with the oxygen. Under those conditions, of course, heavy scale would interfere with this metal surface reaction.

K. R. VAN HORN:[5] I would like to ask a question regarding Mr. Sim's

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[2]Westinghouse Electric and Manufacturing Co., E. Pittsburgh, Pa.
[3]International Nickel Company, Bayonne, N. J.
[4]American Steel Foundries, Research Laboratories, Indiana Harbor, E. Chicago, Indiana.
[5]Aluminum Co. of America, Cleveland.

remarks on the explanation for greater decarburization in coarse-grained than in fine-grained steels. The argument proceeds very well until the conclusion, and it would seem that the reverse should exist. Single crystals of iron, copper, aluminum, and most metals have very slow diffusion rates, whereas polycrystalline material is characterized by faster diffusion rates. In the fine-grained steels there would be more rapid diffusion than in coarse-grained steels, so that fine-grained steels, if diffusion were the explanation, should have greater surface decarburization than coarse-grained steels. This is not, of course, the case, as is demonstrated by experiments of the authors and by those of numerous others, so another explanation would be welcome.

In answer to both questions, one refers to an atmosphere of hydrogen, and the other to the fact that most metals having fine grains have faster diffusion rates than coarse grains. In commercial fine-grained steel products, such as forgings and rolled shapes, shorter annealing times are employed than for steel castings, and the reason is that greater diffusion is possible in fine-grained material which consists of a larger number of grain boundaries and disoriented material which would facilitate diffusion.

PROFESSOR UPTHEGROVE: We appreciate having Mr. Jominy call our attention to the relation of scaling in decarburization because that is something we are inclined to forget at times. He raises the question as to whether or not any other substances can be used in place of hydrogen and also mentions that nitrogen with moisture is a very effective decarburizer. We are doing work along the lines suggested by Mr. Jominy. In one or two instances we actually have found greater decarburization where we have used moist nitrogen than we did with the moist hydrogen, but that is only in a few cases. Some of the other questions that were raised by Mr. Jominy, have been more or less answered by the various discussers.

Dr. Yensen raises the question as to whether or not the decarburization takes place at the surface, and refers to Mr. Jominy's statement.

However, I believe I am correct in interpreting Mr. Jominy's statement not to that effect, but rather that the decarburization takes place at an interface within the steel, and not at the surface, because he speaks of the penetration of the gas and does not state how the gas gets in. In Fig. 30, we have a sample decarburized for twenty-five hours at 1410 degrees Fahr. and quenched directly from the decarburizing operation. It does not show quite all of the sample. It was necessary to do a little readjustment and we did not get the top section in. However, you will notice that we have in the upper portion a very definite ferrite band, corresponding to this low zone of carbon, and below that we have a zone which is martensitic to troostitic. It would seem that this indicates definitely that there is a reaction interface. If you will examine some of the other photomicrographs, you will find that very fine ferrite crystals are precipitated at this interface. It indicates that such an interface exists, and that the reaction is not taking place at the surface.

The discussion with regard to diffusion in a way indicates why we took up this particular problem—that is, does diffusion take place by means of the grain boundaries or through the grains themselves? In answer to Mr. French's question, we would say that we believe that the diffusion inward of the decarburizing agent is by means of travel through the grains, and not

along the grain boundaries. That would account for the greater ease of decarburization of the coarse-grained steel over the fine-grained steel, while if diffusion took place along the grain boundary it should travel more readily through the fine grains because there is much more boundary material than with the coarse-grained steel.

Authors' Written Closure

The authors appreciate very fully the comments of Dr. C. R. Austin. He raises a question as to the advisability of not having included a means of removing nitrogen in the purification train. Inasmuch as the primary object of the investigation was to determine the effect of grain-size and three samples of fine- and coarse-grained steels of a like carbon content were to be run simultaneously in an atmosphere of hydrogen saturated with water vapor, it was felt that the presence of very small quantities of nitrogen could have no bearing on the results. It is true that at times a very slight staining of the stainless steel was obtained. The three specimens run simultaneously were as near alike in carbon content as could be obtained from regular production.

In referring to Dr. Austin's work on decarburization of steel with dry hydrogen it was not the intention to infer that his results for 800 degrees Cent. (1470 degrees Fahr.) held for all temperatures. However, as pointed out by Dr. Austin, "early experiments also demonstrated that ordinary dry hydrogen decarburized so slowly that at 775 or 950 degrees Cent. (1425 or 1740 degrees Fahr.), even after several hours of test, chemical analysis was necessary to establish definitely a reduction in peripheral carbon content."

Dr. Austin's suggestions relative to the possible significance of the practically constant concentration of methane and the progressive decrease in the carbon monoxide contents of the gaseous products of the decarburization are extremely interesting. The CH_4 curves, while found to be straight lines, may have a slight curvature but the method of analysis was not delicate enough to detect such curvature. A curvature does not of a necessity exist, however, since there are a number of possible reactions involving CH_4 which mitigate towards its decomposition, and equilibrium conditions within the furnace may well be such as to reduce the percentage of CH_4 in the exit gases to a constant value for any given temperature. Because of the reactions mentioned it is probable that the formation of CH_4 takes place neither at the gas-metal interface nor within the ferrite band, but within the higher carbon zone—possibly at the junction of the partially decarburized area and the ferrite band.

The carbon monoxide concentration curves are undoubtedly the results of processes dependent upon the laws of gaseous and solid diffusion.

Mr. Sims has raised the question as to the existence of an interface within the steel at which the reaction between oxygen and carbon can take place. He states that the diffusion of molecular CO seems to be almost ruled out in the rate of decarburization that is obtained. Recent work of L. N. Khitrin, however, indicates that CO has a comparatively high diffusion rate in steel. He found that CO and H_2 both diffuse strongly and almost equally at as low as 300 degrees Cent. (570 degrees Fahr.). Rates of diffusion increase rapidly with increasing temperatures.

Mr. Sims has also pointed out the absence of visible iron oxide particles in the surface ferrite of some of the photomicrographs showing the decarburization. The work of Tritton and Hanson is interesting in this connection. In their investigations of iron and oxygen they refer to the possible solubility of oxygen in iron and to the amount of oxide necessary for it to be visible under microscopic examination. They state that the solubility is estimated at about 0.05 per cent and that it seems likely that no oxide should be visible if 0.05 per cent or less were present. Under the conditions assumed for the occurrence of decarburization of the steel, it is not necessary that iron oxide be present in excess of 0.05 per cent. As to whether or not the heavily scaled steel has decarburized to a lesser extent than the one only slightly scaled, the question must be raised to what extent has the metal been removed by the scaling of the steel?

Dr. Van Horn has stated that polycrystalline material usually has faster diffusion rates than single crystals of metals and that therefore the fine-grained steels should decarburize more readily than coarse-grained steels if diffusion were the explanation. This not being the case, some other explanation is required. He also refers to shorter annealing times required for rolled shapes as compared to castings. Dr. Van Horn's point may perhaps best be answered by raising the question, are the conditions for the establishment of the above differences in diffusion similar to the conditions existing in the decarburization of steel and are the diffusion phenomena similar? It would seem not for if they were, then the established differences in the depth of penetration in the carburization of fine- and coarse-grained steels could not be accepted as diffusion phenomena.

PICKLE PITTING BY ELECTROLYTIC POTENTIALS AS AFFECTED BY SCALING TEMPERATURE

By C. H. McCollam and D. L. Warrick

Abstract

Pickle pitting is frequently caused by an electrolytic couple, set up between scale-free areas and scale formed above a certain critical temperature. This critical or transition temperature varies with steels of different compositions. When scale is formed below the transition temperature, neither the difference in electrical potential nor the depth of pitting from this cause are significant. When this temperature is exceeded, the difference in potential, found to be approximately 0.6 volt, results in a galvanic action between the scale and the metal, which proceeds at the expense of the metal. The magnitude of the resulting pit is a function of time and current density.

The effect of mechanical scale breaking, electrolytic pickling, and pickling inhibitors on this type of pitting is discussed.

PICKLE pitting of steel may be defined as localized attack during the pickling operation, resulting in surface pits of various sizes and depths. Typical examples will be seen in Figs. 1 and 2. Over-pickling is evidenced either by a more or less uniform reduction in section of the material or by the appearance of porosity on the pickled surface. This porosity appears first on the transverse surfaces. An insight into the basic difference between these two pickling defects may be gained from the observation that over-pickling is a function of the latter part of the pickling cycle only, while pickle pitting generally (though not always) has its inception during the earlier part of the pickling operation.

Pickling of alloy steels is accompanied by certain difficulties which are aggravated by the time and temperature required to remove the scale from the various alloy types. This is particularly true of scale removal after certain heat treating operations. Improved supervision and the use of inhibitors have largely eliminated over-pickling, but pickle pitting has been found to be less responsive. During a

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recent investigation of pickling defects, the authors of this paper had the opportunity to identify several causes of pickle pitting. One of these causes, which is apparently quite prevalent, was studied in some detail and the results are reported herein.

Preliminary Observations

Deep surface pitting had been consistently reported on certain pearlitic alloy steels pickled after annealing. Examination of the pitted steels showed that the smaller areas of about ½ inch in diameter were pitted deeply, while on larger areas the depth of pitting was less pronounced, an inverse ratio apparently existing between the size of the area and the depth of the pitting.

It was suspected that these pitted areas represented surfaces from which the scale had been broken off before pickling. To confirm this supposition tests were made on sample pieces of annealed tubing taken from commercial production. Scale was purposely removed to expose areas of several sizes on the different tube samples before pickling and the clean areas outlined with punch marks. Examination of the tube samples after pickling showed the pitted areas to lie within the punch marks, proving the correctness of the earlier observations. Hot-rolled tubes from this lot were pickled before annealing and showed no pitting. This seemed to indicate that the cause of pitting was not inherent in the steel nor the result of rolling or piercing. The pickling acid carried an inhibitor that had proven reasonably satisfactory, furthermore, it had not pitted the hot-rolled material.

The boundary of the pitted area was frequently marked by a deep, narrow line of demarcation, indicating that the action was of an electrolytic nature. This was thought to be a function of the difference in potential between the scale and the scale-free areas during the pickling operation. In order to check this theory a program was inaugurated, first to establish a procedure for measuring the differences in electrical potential between metal and scale formed at various temperatures, then to correlate these differences with the surface characteristics of the steels after pickling. The method of procedure adopted and results obtained are described.

Materials

The steels selected for these tests (Table I) included S.A.E.

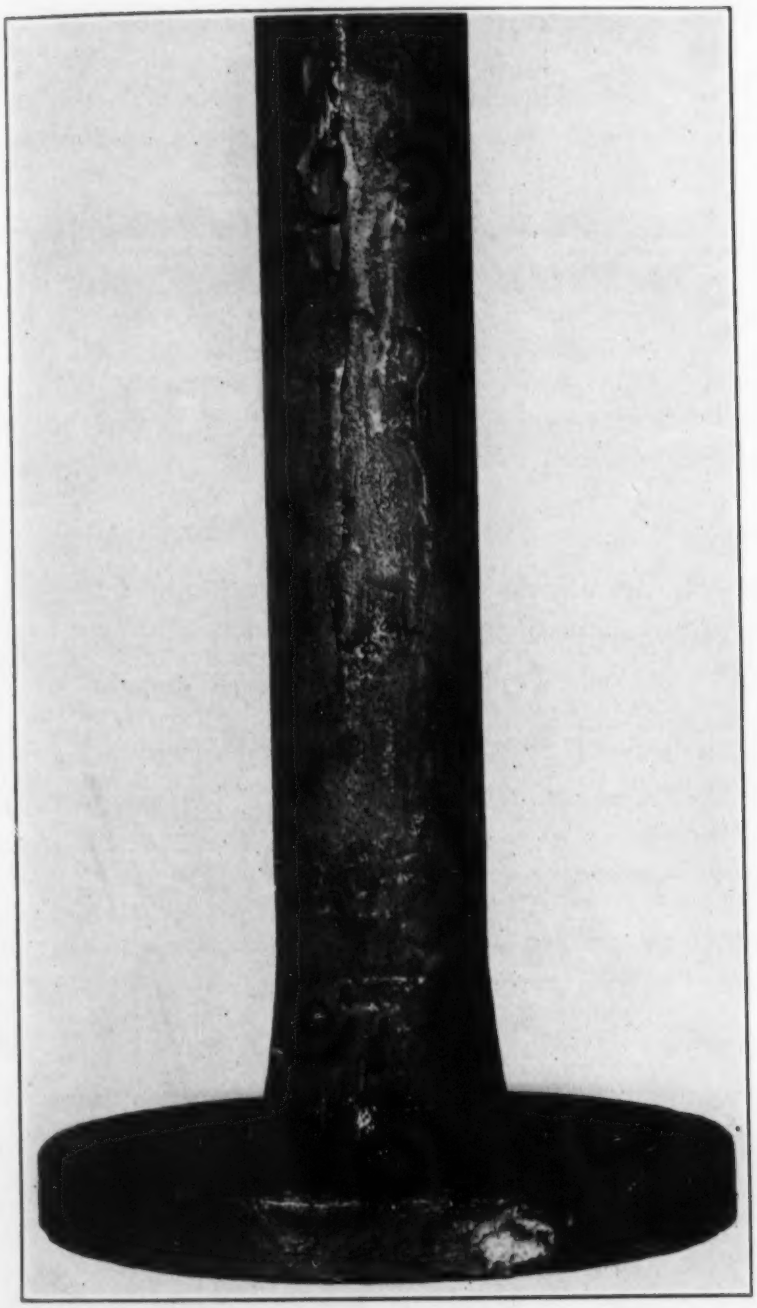


Fig. 1—Typical Pickle Pitting on Forged and Normalized Axle Shaft.

4615, S.A.E. 52100 and a carbon-molybdenum steel. They were chosen for their diversity of composition as well as for their wide use in the automotive and other industries, where surface finish and size

are important considerations. A few tests were later made on S.A.E. 3115.

A study of additional steel types to determine the relation of various carbon and alloy contents to behavior in pickling would un-

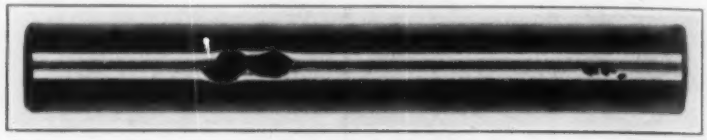


Fig. 2—Pickle Pits in Centerless Ground Stock.

doubtedly be of interest, but it seemed impracticable to examine a large number of alloy compositions at one time.

Apparatus

Samples were scaled in an electrically heated laboratory muffle furnace, inside dimensions 12 by 6 by 4 inch. Furnace temperature was regulated by a controlling potentiometer, using a chromel-alumel thermocouple. Maximum deviation was about ± 15 degrees Fahr.

Equipment for the measurement of potentials consisted of a galvanometer of the portable pointer type, having a sensitivity of 0.5

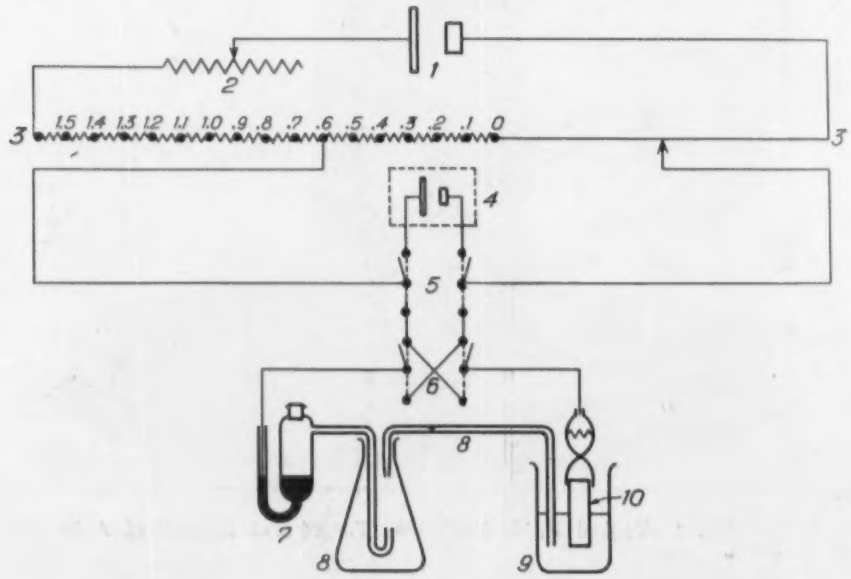


Fig. 3—Diagram of Apparatus for Potential Measurements.

1. Battery.
2. Calibrating Rheostat.
3. Potentiometer.
4. Standard Cell.
5. Double Pole, Double Throw Switch.
6. Reversing Switch.
7. Calomel Electrode.
8. Salt Water Bridge.
9. Acid Sol. Containing 1% $FeSO_4$.
10. Steel or Scaled Sample.

Table I
Chemical Analysis of Steels

Steel Type	Per Cent							
	Carbon	Manganese	Phosphorus	Sulphur	Silicon	Chromium	Nickel	Molybdenum
S.A.E. 4615	0.17	0.60	0.020	0.020	0.25	0.15	1.70	0.23
S.A.E. 52100	1.00	0.32	0.018	0.018	0.30	1.45	0.15	...
Carbon-Molybdenum	0.63	0.75	0.015	0.015	0.25	0.08	0.15	0.23

milliamperes, a standard cell, and a normal calomel electrode. A reversing switch was included in the circuit for convenience in measuring potentials that were either positive or negative to the calomel electrode. A diagram of the hook-up used for making the measurements is shown in Fig. 3.

Method of Procedure

Preparation of Samples

Samples for the pickling tests and the measurements of electrolytic potential were machined to 1-inch round from 1¼-inch round annealed bars and cut into 3-inch lengths with a high speed carborundum cutting wheel. A limited amount of preliminary work had shown no appreciable difference in potential between smooth machined and ground surfaces before scaling, and only slight differences after scaling (Table II). Machined samples were therefore selected as being easier to produce than ground samples.

Method of Scaling

Samples were placed upright in the muffle furnace and pre-

Table II
Effect of Surface Preparation
S.A.E. 52100 Steel

Surface	Scaling Temperature	Time of Scaling	Kind of Acid*	Potential in Millivolts**
Ground	.....	.....	H_2SO_4	−524
Machined	.....	.....	H_2SO_4	−523
Ground	.....	.....	Sludge	−485
Machined	.....	.....	Sludge	−475
Ground	1400 degrees Fahr.	16 hours	H_2SO_4	−396
Machined	1400 degrees Fahr.	16 hours	H_2SO_4	−446
Ground	1400 degrees Fahr.	16 hours	Sludge	−389
Machined	1400 degrees Fahr.	16 hours	Sludge	−437

*7.6 per cent acid containing 1 per cent $FeSO_4$ at 70 degrees Fahr.
**Normal calomel electrode potential taken as zero.

cautions taken to insure uniform heating and to prevent the pieces from touching each other. Six samples were charged in the cold furnace and brought to the designated temperature as rapidly as possible; temperature was maintained for 16 hours by automatic controller, after which the samples were furnace cooled with the door open. By this method an unbroken scale of considerable thickness was obtained that served as a satisfactory electrode for the measurement of potentials.

Each furnace charge was composed of samples of one steel only, and samples of each steel were scaled at each temperature of test. A range of temperatures from 1300 to 1800 degrees Fahr. (705-980 degrees Cent.) by intervals of 100 degrees Fahr. was arbitrarily chosen, as representing approximately the range of commercial heat treating temperatures. Tests were also made at a few intermediate points to approximate the transition temperatures of the S.A.E. 52100 and carbon-molybdenum steels.

Two of the six samples in each furnace charge were pickled to determine the effect of scaling temperature on the pickled surface, two more were used as electrodes in measuring the electrolytic potential of the scaled layer, and the remaining two were held as reserve samples.

Pickling Procedure

The two samples from each furnace charge intended for the pickling tests were carefully pickled to establish the effect of scaling temperature on the character of the pickled surface. Prior to pickling, scale was broken off a small area of the sample by a light hammer blow. Two different pickling solutions were used, both having a sulphuric acid concentration of 7.6 per cent by weight, corresponding to 1.56N. One solution was made from 66 degrees Bé acid and the other from a sludge acid that is widely used as a self-inhibited pickling agent.

The temperature of the pickling acid was maintained at 150 degrees Fahr. $\pm$ 2 degrees Fahr. by means of a large water bath equipped with a stirring motor. This temperature was chosen as representing the average temperature for sulphuric acid pickling.

Samples were momentarily removed from the acid at regular intervals for inspection, and when scale removal was complete were rinsed in hot water and wiped dry. The surfaces were inspected with particular attention to the areas from which scale had been

Table III
Effect of Scaling Temperature on Pickling Time and Surface Quality

Steel Type	Scaling Temp. Deg. Fahr.	In Sulphuric Acid*	In Sludge Acid*	Surface Quality
S.A.E. 52100	1300	25	37	Not Pitted
52100	1400	12	14	Not Pitted
52100	1430	23	45	Not Pitted
52100	1460	51	118	Pitted
52100	1500	70**	65**	Pitted
52100	1600	153	148	Pitted
52100	1700	210**	210**	Pitted
52100	1800	210***	210***	Pitted
Carbon-Molybdenum	1300	65	65	Not Pitted
Carbon-Molybdenum	1350	60	60	Slight Pitting
Carbon-Molybdenum	1400	60	90	Pitted
Carbon-Molybdenum	1500	120	135	Pitted
Carbon-Molybdenum	1600	180	180	Pitted
Carbon-Molybdenum	1700	230	230	Pitted
Carbon-Molybdenum	1800	220	220	Pitted
S.A.E. 4615	1300	55	55	Lightly Pitted
4615	1400	70	75	Lightly Pitted
4615	1430	90	90	Lightly Pitted
4615	1460	90	90	Pitted
4615	1500	105	105	Pitted
4615	1600	135	90	Pitted
4615	1700	85	95	Pitted
4615	1800	60	90	Pitted

*7.6 per cent acid solutions at 150 degrees Fahr.
**Nearly complete.
***Incomplete.

removed before pickling. Figs. 4 to 9 show typical scaled and pickled test pieces, the complete data on the pickling tests being presented in Table III.

Measurement of Potentials

Two scaled samples from each furnace charge were used as electrodes for measurements of potential differences. A strong battery clip supported the sample in the electrolyte and served as a connector. To insure contact of the clip with the metal, scale was removed from this end of the sample by grinding. As a further precaution, the connection was always made on the end of the sample that had been resting on the furnace floor during scaling. Depth of immersion was 1½ inches.

The electrolyte solutions finally adopted were made by adding 1 per cent of ferrous sulphate to the pickling solutions previously described.

Preliminary attempts to obtain the difference in potential between scale and steel electrodes by direct measurement were unsuccessful, probably due to rapid polarization of the electrodes as they

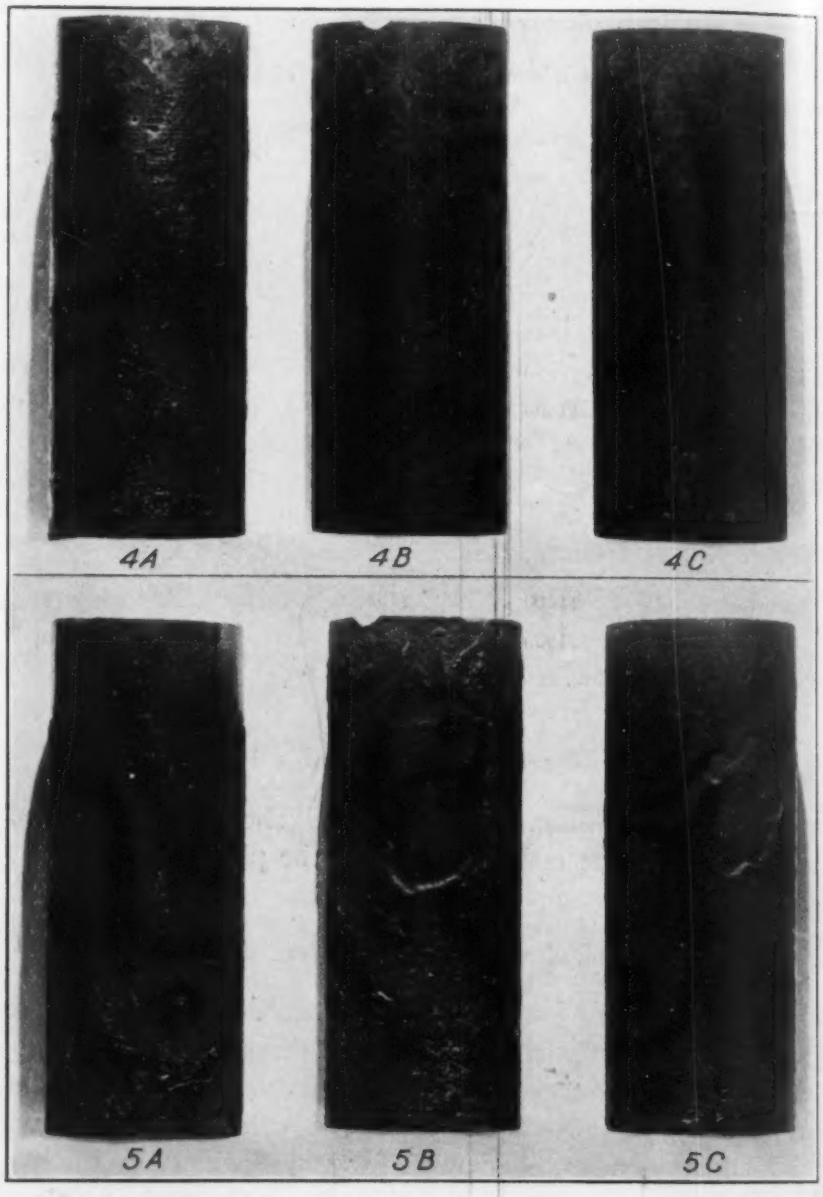


Fig. 4—Samples of S.A.E. 52100 Steel Scaled 16 Hours in Air at 1400 Degrees Fahr. (760 Degrees Cent.). Potential of Scale to Steel 70 Millivolts. 4A—Scaled Sample; 4B—Pickled in Sulphuric Acid—No Pitting; 4C—Pickled in Sludge Acid—No Pitting.

Fig. 5—Samples of S.A.E. 52100 Steel Scaled 16 Hours in Air at 1500 Degrees Fahr. (815 Degrees Cent.). Potential of Scale to Steel 565 Millivolts; 5A—Scaled Sample; 5B—Pickled in Sulphuric Acid—Pitted; 5C—Pickled in Sludge Acid—Pitted.

went into solution in the electrolyte. The potential of the scaled samples and the steel electrodes was therefore determined separately against a normal calomel half-cell as a reference electrode, and the

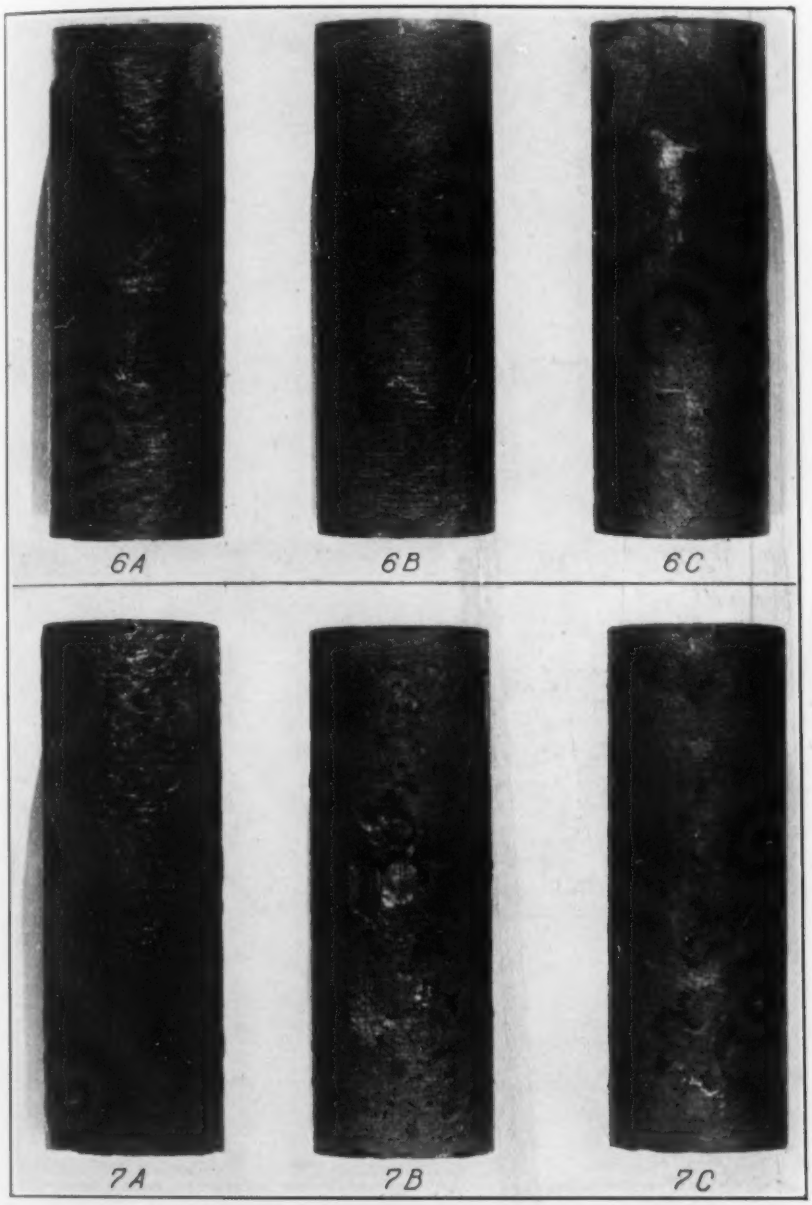


Fig. 6—Samples of Carbon-Molybdenum Steel Scaled 16 Hours in Air at 1300 Degrees Fahr. (705 Degrees Cent.). Potential of Scale to Steel 225 Millivolts. 6A—Scaled Sample; 6B—Pickled in Sulphuric Acid—No Pitting; 6C—Pickled in Sludge Acid—No Pitting.

Fig. 7—Samples of Carbon-Molybdenum Steel Scaled 16 Hours in Air at 1500 Degrees Fahr. (815 Degrees Cent.). Potential of Scale to Steel 666 Millivolts. 7A—Scaled Sample; 7B—Pickled in Sulphuric Acid—Badly Pitted; 7C—Pickled in Sludge Acid—Pitted.

difference in electrical potential calculated by algebraic difference.

Until ferrous sulphate was added to the electrolyte, readings of potentials were found to change very rapidly while tests were in

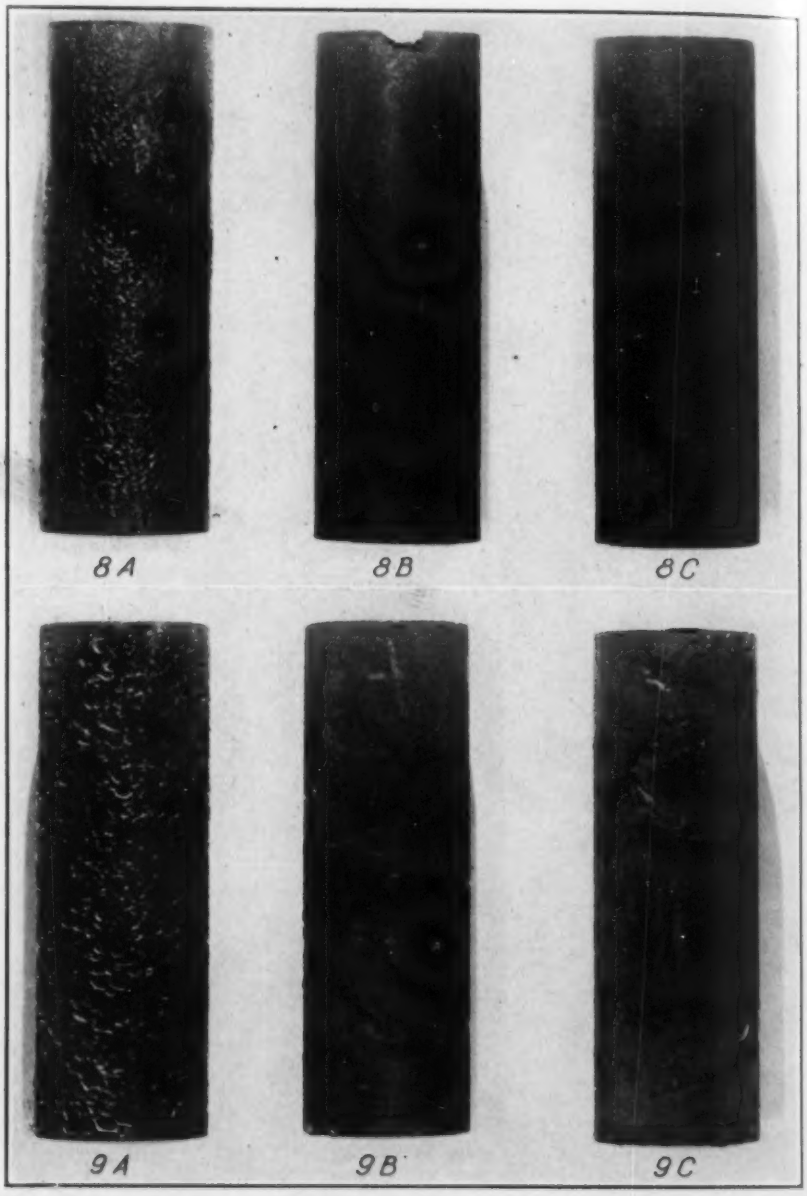


Fig. 8—Samples of S.A.E. 4615 Steel Scaled 16 Hours in Air at 1400 Degrees Fahr. (760 Degrees Cent.). Potential of Scale to Steel 290 Millivolts. 8A—Scaled Sample; 8B—Pickled in Sulphuric Acid—Slightly Pitted; 8C—Pickled in Sludge Acid—Slightly Pitted.

Fig. 9—Samples of S.A.E. 4615 Steel Scaled 16 Hours in Air at 1500 Degrees Fahr. (815 Degrees Cent.). Potential of Scale to Steel 500 Millivolts. 9A—Scaled Sample; 9B—Pickled in Sulphuric Acid—Pitted; 9C—Pickled in Sludge Acid—Pitted.

progress, beginning immediately after immersion of the sample in the electrolyte. In a straight acid electrolyte, the action of the pickling acid frequently produced an appreciable change in the appear-

ance of the electrode before a constant potential was reached. It seemed probable in the circumstances that this change in potential followed the rapid initial change in ferrous ion concentration of the fresh electrolyte in the vicinity of the electrodes followed by a more gradual change in potential as the ferrous ions in solution became numerous. (The potential varies as the logarithm of the concentra-

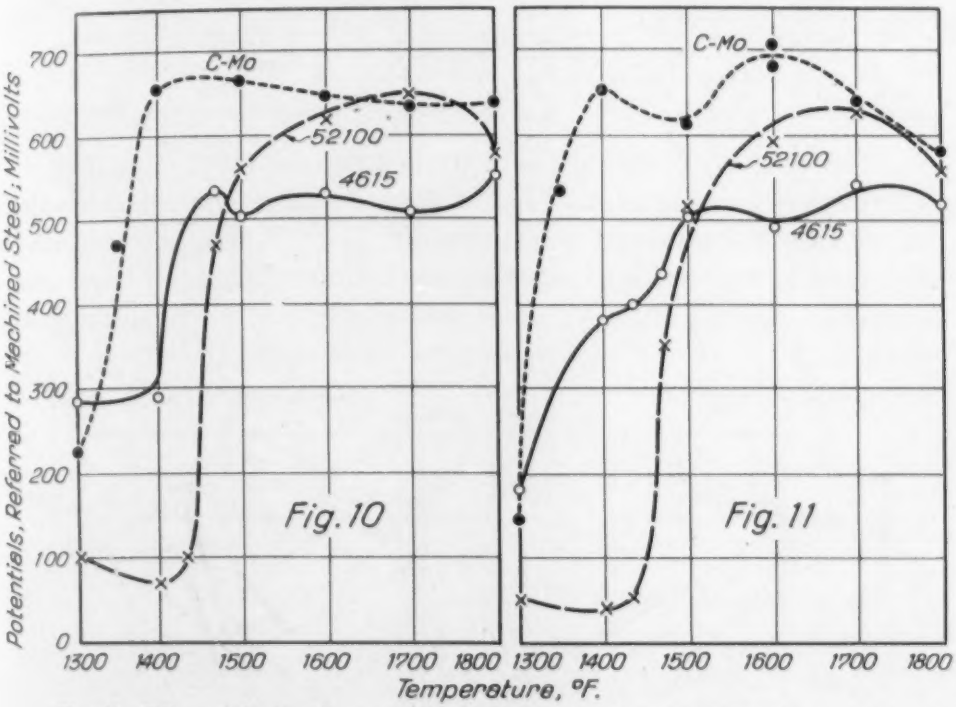


Fig. 10—Effect of Scaling Temperatures on Potentials of Scaled Electrodes in Sulphuric Acid.

Fig. 11—Effect of Scaling Temperatures on Potentials of Scaled Electrodes in Sludge Acid.

tion of ferrous ions in the electrolyte.) The addition of 1 per cent of ferrous sulphate was found to stabilize the electrolyte by supplying the necessary ferrous ion concentration, and as a consequence the change during reading of potentials was less pronounced.

A gradual increase or decrease of potential depending on the sample was still found with the electrolyte finally adopted. Potentiometer readings were therefore recorded at intervals of one minute during the first five minutes of immersion. To avoid the variations sometimes present in the initial readings, the value recorded at the second minute was used in Figs. 10 and 11. Typical values for potentials of machined steel through the five minute periods are given in Table IV.

Table IV
Effect of Immersion Time on Potentials of Machined Steels

Steel Type	Acid** Used	Potentials * in Millivolts 1st Minute	2nd Minute	3rd Minute	4th Minute	5th Minute
S.A.E. 52100	Sulphuric	—537	—533	—529	—525	—520
52100	Sludge	—486	—486	—486	—486	—485
S.A.E. 4615	Sulphuric	—570	—570	—574	—574	—574
4615	Sludge	—537	—545	—553	—557	—560
Carbon-Molybdenum	Sulphuric	—530	—530	—530	—530	—530
Carbon-Molybdenum	Sludge	—484	—488	—491	—495	—495

*Normal calomel electrode potential taken as zero.
**7.6 per cent acid containing 1 per cent of $FeSO_4$.

The electrolyte was at room temperature in these experiments. An electrolyte temperature of 150 degrees Fahr. seemed desirable for making the potential measurements, since it was the temperature used in the pickling experiments. Many difficulties were encountered, however, in attempting measurement of potentials at this temperature, so that it was decided to leave the electrolyte at room temperature.

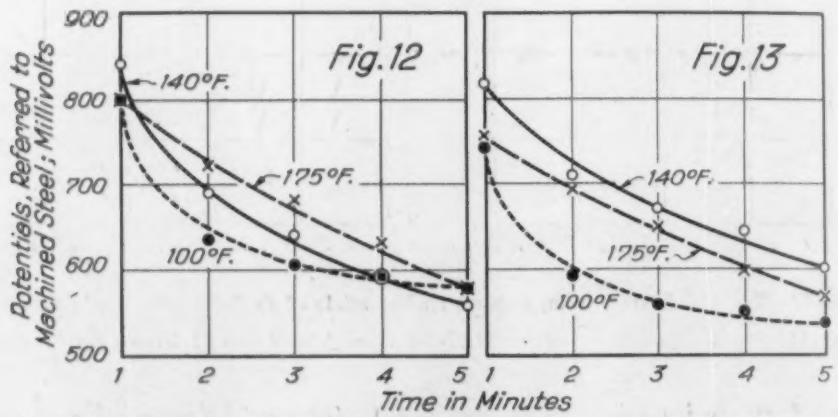


Fig. 12—Differences of Potentials at Various Temperatures of the Electrolyte. S.A.E. 3115 Steel in Sulphuric Acid.
Fig. 13—Differences of Potentials at Various Temperatures of the Electrolyte. S.A.E. 3115 Steel in Sludge Acid.

A limited amount of experimental work indicated that while the potentials of the individual samples are not the same at different electrolyte temperatures, the general relationship of potential values to scaling temperatures is essentially the same regardless of the electrolyte temperatures. Table V and Figs. 12 and 13 show data for S.A.E. 3115 steel scaled at 1600 degrees Fahr. (870 degrees Cent.) with the temperature of the electrolyte varying from 100 to 175 degrees Fahr.

Table V

Effect of Electrolyte Temperatures on Steel and Scale Potentials.
S.A.E. 3115 Steel

Scaling Temperature	Acid Used**	Acid Temp. Deg. Fahr.	Potential * in Millivolts 1st Minute	2nd Minute	3rd Minute	4th Minute	5th Minute
Machined	Sulphuric	100	−497	−502	−503	−504	−504
Machined	Sulphuric	140	−502	−509	−509	−509	−509
Machined	Sulphuric	175	−496	−502	−506	−506	−505
Scaled (1600 degrees Fahr.)	Sulphuric	100	301	131	102	87	70
Scaled (1600 degrees Fahr.)	Sulphuric	140	332	181	131	84	48
Scaled (1600 degrees Fahr.)	Sulphuric	175	301	211	175	125	74
Machined	Sludge	100	−439	−441	−444	−448	−449
Machined	Sludge	140	−489	−489	−493	−505	−510
Machined	Sludge	175	−475	−485	−492	−497	−501
Scaled (1600 degrees Fahr.)	Sludge	100	310	151	117	102	86
Scaled (1600 degrees Fahr.)	Sludge	140	330	220	175	140	88
Scaled (1600 degrees Fahr.)	Sludge	175	279	205	153	97	65

*Normal calomel electrode potential taken as zero.
**7.6 per cent acid by weight, with 1 per cent $FeSO_4$.

Table VI

Effect of Scaling Temperature on Potential Difference Between Steel and Scale*
S.A.E. 52100 Steel

Scaling Temperature Deg. Fahr.	Acid Used**	Potential Difference in Millivolts 1st Minute	2nd Minute	3rd Minute	4th Minute	5th Minute
1300	Sulphuric	119	100	92	88	78
1400	Sulphuric	100	70	65	62	57
1430	Sulphuric	187	100	79	67	68
1460	Sulphuric	467	476	267	162	156
1500	Sulphuric	581	565	551	525	479
1600	Sulphuric	642	620	599	582	564
1700	Sulphuric	657	651	640	627	608
1800	Sulphuric	617	577	533	442	282
1300	Sludge	57	49	43	42	42
1400	Sludge	49	23	16	14	14
1430	Sludge	58	28	19	14	13
1460	Sludge	420	346	263	237	224
1500	Sludge	...	515	492	469	445
1600	Sludge	609	587	565	552	534
1700	Sludge	644	630	608	582	566
1800	Sludge	...	560	534	503	460

*Based on the potential of machined S.A.E. 52100 Steel at the same time interval.
**7.6 per cent acid containing 1 per cent $FeSO_4$.

General Considerations

It will be seen in Tables VI, VII and VIII that at heat treating temperatures below 1500 degrees Fahr. (815 degrees Cent.) there is a temperature interval through which the difference in potential between the scale and the clean metal shows an abrupt rise. This rise does not occur at exactly the same temperature for all steels. Above 1500 degrees Fahr. (815 degrees Cent.) a considerably higher poten-

Table VII
Effect of Scaling Temperature on Potential Difference Between Steel and Scale*
S.A.E. 4615 Steel

Scaling Temperature Deg. Fahr.	Acid Used**	1st Minute	2nd Minute	3rd Minute	4th Minute	5th Minute
1300	Sulphuric	...	286	240	188	171
1400	Sulphuric	208	290	193	193	193
1430	Sulphuric	455	397	289	215	207
1460	Sulphuric	560	538	528	502	484
1500	Sulphuric	541	500	479	459	451
1600	Sulphuric	538	524	512	499	490
1700	Sulphuric	502	507	517	520	525
1800	Sulphuric	540	552	558	559	557
1300	Sludge	...	215	195	142	114
1400	Sludge	352	311	449	487	515
1430	Sludge	455	397	289	215	207
1460	Sludge	560	538	528	502	484
1500	Sludge	536	503	497	487	477
1600	Sludge	509	493	493	463	451
1700	Sludge	525	542	554	562	570
1800	Sludge	503	522	534	534	538

*Based on the potential of machined S.A.E. 4615 steel at the same time intervals.
**7.6 per cent acid by weight, with 1 per cent $FeSO_4$.

tial difference was found, the difference being approximately 0.6 volt.

The general appearance of the scale likewise seems to undergo a change as the scaling temperature is increased. This was particularly noticeable in the case of the S.A.E. 52100 samples, on which the scale formed at temperatures up to and including 1430 degrees Fahr. (775 degrees Cent.) was comparatively thin and porous.

The outer layer was reddish brown in color. Beneath this was a thin black layer with another reddish brown layer next to the metal. At temperatures of 1460 degrees Fahr. (795 degrees Cent.) and above the outside layer became black, the reddish hue appearing only in the layer next to the metal. Above 1500 degrees Fahr. (815 degrees Cent.) the red color disappeared altogether. Scale formed at 1460 degrees Fahr. (795 degrees Cent.) or above had a hard glassy texture which was quite adherent and relatively nonporous. As might be expected, the layers of scale grew progressively thicker as the scaling temperature increased. The scaling medium which in this investigation was air, undoubtedly had an influence on the color and texture of the scale formed.

The close proximity of the transition temperatures to the Ac points of the steels used in this investigation is apparent (Tables VI, VII and VIII). It is reasonable to expect that some relation between these phenomena might exist. The transition temperatures and rise

in potential difference are less sharply defined, however, in the case of the S.A.E. 4615 steel than for the other steels.

Probably the change in potential is associated with a change in chemical composition of the scale, which in this case would mean a change in the state of oxidation of the surface layers of the electrode. In other words, we might expect the ratios of the ferric, ferrous and free iron to be altered as the scaling temperature is changed. Various observers have held that iron oxide scale is not a simple substance, but is composed of different proportions of Fe_2O_3, Fe_3O_4, FeO and Fe. Furthermore, it is generally accepted that a piece of steel in a state of complete oxidation is covered by several layers of scale rather than by a single homogeneous layer. Since a state of complete equilibrium in the scale is not attained during the heat treating operation, rates of reaction or diffusion, or both, are important factors in determining the composition of the scale at any point.

A direct comparison of the results presented herein with those of other investigators is rendered difficult by the fact that a large portion of the work reported in the literature deals with carbon steels, while this study has been confined to alloy types. An interesting comparison is noted however, between Figs. 10 and 11 of this paper, and a graph presented by C. Upthegrove,[1] showing the relation

Table VIII

Effect of Scaling Temperature on Potential Difference Between Steel and Scale* Carbon-Molybdenum Steel

Scaling Temperature Deg. Fahr.	Acid Used**	Potential Difference in Millivolts 1st Minute	2nd Minute	3rd Minute	4th Minute	5th Minute
1300	Sulphuric	403	225	189	172	176
1350	Sulphuric	533	473	398	303	238
1400	Sulphuric	709	657	642	636	632
1500	Sulphuric	723	666	666	663	657
1600	Sulphuric	685	666	665	663	661
1700	Sulphuric	635	633	631	627	622
1800	Sulphuric	635	635	635	630	629
1600	Sulphuric	793	755	747	740	736
1300	Sludge	195	145	141	141	141
1350	Sludge	563	523	504	484	464
1400	Sludge	729	655	631	624	617
1500	Sludge	643	613	606	603	595
1600	Sludge	712	680	658	653	644
1700	Sludge	642	640	645	651	653
1800	Sludge	580	585	586	587	583
1600	Sludge	738	709	704	704	704

*Based on the potential of machined carbon molybdenum steel at the same time interval.
**7.6 per cent acid by weight, containing 1 per cent $FeSO_4$.

[1]Clair Upthegrove, University of Michigan Engineering Research Bulletin No. 25.

between scaling temperature and the percentage of ferrous iron in the scale. In both cases marked changes in the slope of the curves appear at about 1500 degrees Fahr. (815 degrees Cent.) and again near 1800 degrees Fahr. (985 degrees Cent.).

Knowledge of the potentials of electrodes made from pure Fe_2O_3, Fe_3O_4 and FeO should prove interesting, but our primary interest lay in the heterogeneous mixtures formed when steels are

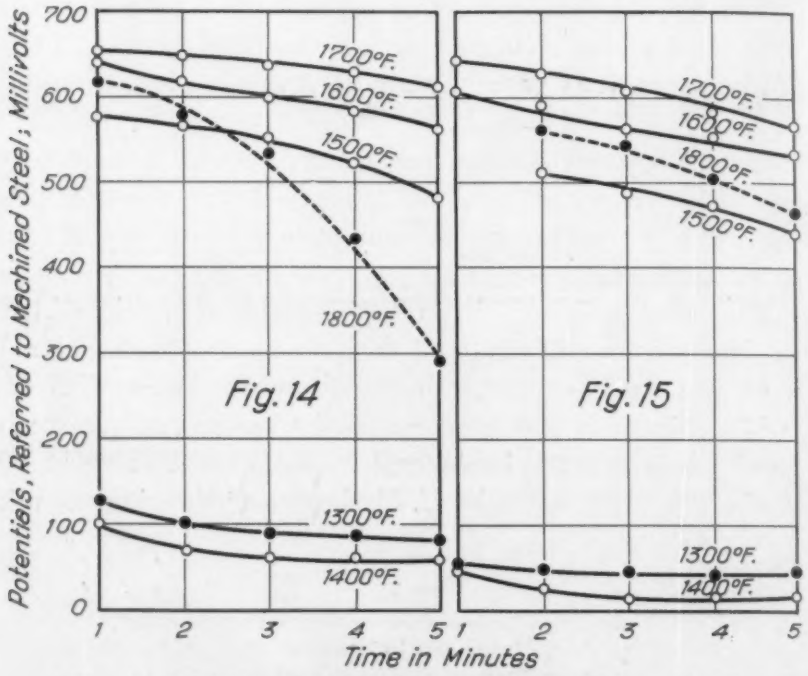


Fig. 14—Variation of Potentials of Scaled Electrodes with Time of Measurement. S.A.E. 52100 Steel in Sulphuric Acid.
Fig. 15—Variation of Potentials of Scaled Electrodes with Time of Measurement. S.A.E. 52100 Steel in Sludge Acid.

heated under oxidizing conditions, with the purpose of establishing causes and possible remedies for prevalent pickling difficulties. Extensive researches of a more academic nature would be necessary to complete the information on the subject.

The causes for the observed change of potential values with time of electrode immersion have not been definitely established. Under the conditions of the tests, possible explanations for this behavior might include:

(1) Progressive polarization of the electrodes due either to deposition of some substance on the surface or to selective dissolution of the electrode with resulting change in the surface character.

(2) Diffusion of the electrolyte through the scale layer, re-

sulting in an increasing number of direct contacts between electrolyte and steel, the effective electrode becoming a composite mixture of minute areas of scale and steel. It was observed that the electrolyte showed a tendency to creep up through the unimmersed portion of the scaled layer. This was particularly noticeable with samples scaled in the lower temperature ranges. Surface wetting at times extended as far up as the clip used to hold the sample. However, this did not occur within the five minute period during which potential values were being recorded.

Whatever the real cause of this change in potential values may be, it should be remarked that the amount of such change was generally small in proportion to the total change that occurs in the transition range. Figs. 14 and 15 show a graphical presentation of a typical set of such values. Wide deviations from the mean seldom occur, and when observed are near the beginning or end of the five minute period of readings. For this reason values taken at the end of the second minute were selected as being indicative of the general trend, and used in preparing Figs. 10 and 11.

In presenting measurements of electrical potential values, the authors wish to call attention to the fact that these figures are accurate only within the limits of the equipment at hand. The magnitude of the change in voltage is so great and the transitions are so sharp that their existence is unmistakable. Owing to the recognized difficulties associated with accurate measurement of electrolytic potentials, these admittedly are not precisely correct in every detail.

Discussion of Results

It is apparent from the above results that pickle pitting is frequently caused by an electrolytic couple, set up between scale-free areas and scale formed above a certain critical temperature. This critical or transition temperature varies with steels of different compositions. When scale is formed below the transition temperature, neither the difference in electrical potential nor the depth of pitting from this cause are significant. When this temperature is exceeded the difference in potential, found to be approximately 0.6 volt, results in a galvanic action between the scale and the metal, which proceeds at the expense of the cleaned metal surface. This action continues throughout the pickling cycle until scale removal is complete. The magnitude of the resulting pit is a function of time and current density.

In the past, this type of pitting has been generally attributed either to some inherent defect in the steel, such as segregation or inclusions, or to a defect resulting from fabrication, such as rolled-in scale, the presence of surface strains, et cetera. These factors may at times have certain effects; furthermore, it is understood that there are other causes for pickle pitting than the one described in this paper. We believe, however, that galvanic action is the basic cause of many of the more serious pickling defects. It has been demonstrated that the occurrence of such pitting is reproducible, and that the point at which pitting will occur is predictable.

As was pointed out, the extent to which pitting occurs is a function of time and current density. Any means of reducing either of these factors will tend to alleviate the condition. Thus, by means of mechanical scale-breaking, large areas of clean metal are exposed to the electrolyte and the current density is correspondingly reduced.

An apparent remedy that immediately presents itself is electrolytic pickling. In this process a difference in potential is artificially maintained between two electrodes by an impressed voltage from an exterior source. However, any change in potential on an electrode that is imposed from outside the system becomes effective over the entire surface of the electrode. Therefore, the potentials of scaled and clean areas are raised or lowered alike according to the impressed voltage, but the relative potentials remain the same as before. Since it is the relative difference in potentials of the scale and the metal in contact in the electrolyte that is responsible for the localized action which results in deep pitting, there appears to be little advantage in raising the potential of the electrode as a whole by means of electrolytic pickling.

Another common source of relief from certain pickling defects is the use of inhibitors. The authors conducted a fairly comprehensive study of pickling inhibitors, including their effect on this type of pickle pitting. The photographs in Figs. 4 to 9 show the comparitive effects of uninhibited sulphuric acid and one of the better known inhibited acids. Obviously, the use of an inhibitor has not prevented pitting of the samples in any instance where the potential value was favorable to such action. A pickling inhibitor does not satisfactorily dampen the electrolytic action that is responsible for pickle pitting. After the scale has been removed, the inhibitory effect begins to assert itself, but it is apparent that even then there is a slow preferential

attack of the pitted areas, probably due to the roughened surface of the pit.

Summary

The results of the investigation show:

(1) An important cause of pickle pitting of steel, which occurs frequently in heat treated material, is associated with an electrolytic action between scale and metal in the presence of an acid electrolyte.

(2) The electrolytic potential of the scale is a function of the scaling temperature. Different types of steel behave similarly but not identically.

(3) In the lower range of heat treating temperatures the potential of the scale is only about 0.1 volt higher than that of the metal. No appreciable pitting is likely to occur in such cases.

(4) In the higher range of heat treating temperatures the potential of the scale is about 0.6 volt higher than that of the metal. Deep pitting is likely to occur in such cases.

(5) The transition between these two ranges of temperature is quite sharply defined, and may possibly coincide with the transformation of the steel.

(6) Pickle pits are deepest when very small areas of metal are exposed to the acid for long periods of time while the scale is being removed from the adjacent surface.

(7) Pickling inhibitors may modify this electrolytic action, but the best inhibitors known to the authors do not prevent the deep pitting.

(8) Any method, such as mechanical scale-breaking prior to pickling, which tends to reduce the current density on the exposed areas in the pickling bath, tends to lessen the depth of the pickle pits on the finished product.

Acknowledgment

Special recognition is due J. M. Gotshall who aided the authors with timely suggestions and assisted in all of the experimental work, and to R. L. Wilson for assistance in preparing this paper for publication.

DISCUSSION

O. W. McMULLAN:[1] It is a very interesting paper that the authors have presented, and I was especially interested in the increased depth of the pickle pits with increasing of temperature. In forging and normalizing operations the scale becomes very heavy and it is necessary to keep the parts in the acid a long time, which has to a certain extent eliminated the possibility of pickling as a means of cleaning these parts because of this excessive pitting. This makes necessary the use of more expensive cleaning methods such as sand or shot blasting, or tumbling.

There is one question I would like to ask the authors. They have shown the cause of the deep pitting, but I would like to know if there is anything that can be done to wholly or partially eliminate the action.

F. N. SPELLER:[2] Not having had an opportunity to hear all of this paper or read it, I am hardly able to discuss it in detail. However I might mention some confirmatory experiences of our own. About twenty years ago, we noticed the effect of temperature on the formation and structure of the oxide scale, with regard to the degree of pitting of the metal not only in acids but also when the steel was exposed to water. The potential between scale formed above a certain critical temperature and the steel was markedly greater than where the scale was formed at a lower temperature. Therefore, we designed machinery to remove the thick scale, formed in welding steel pipe at a temperature of about 2400 degrees Fahr. and allowed another scale to form at about 1600 degrees Fahr. The result was that we reduced the damage in acid pickling very materially and the cost of pickling about one-half. We also proved by service tests that the product with the new scale had considerably less tendency to pit where the metal was immersed continuously in domestic water.

V. VOORHEES:[3] I would like to ask a question about the pickling of alloy steel of this type. Why does the scale seem to be so much less soluble in sulphuric acid than the scale of ordinary carbon steel? Apparently a much higher temperature in the pickling bath is necessary to remove it, and this seems to be the main cause of the corrosion of the steel. It is not possible to prevent corrosion of alloy steel by the use of inhibitors to the same extent as is the case with ordinary carbon steel. I hope that the author can give some information on that.

R. E. CHRISTIN:[4] We are rather sorry that the authors have not carried out the test for the chromium-vanadium steels, because our experience has been that this pitting happens more often on the S.A.E. 6130-6140 series. We have noticed without removing mill scale before normalizing that in some instances we have had batches of parts of forgings that have shown pits 100%, and in those cases we have laid it to the fact that the acid bath was weak, because when the acid bath was fresh we found less pitting than when it had been spent. This paper opens up a new idea but it has not covered our point due to the fact that our condition was slightly different. The steel was different, and the forging scale was not removed before the normalizing took place. Like Mr. McMullan we, too, would like to know what can be done about it.

[1]Metallurgist, International Nickel Co., Bayonne, N. J.
[2]Director of Research, National Tube Co., Pittsburgh.
[3]Standard Oil Co. of Indiana, Chicago.
[4]Metallurgist, Columbus Bolt Works, Columbus, Ohio.

Authors' Closure

First, to reply to Mr. McMullan, the ultimate point of this paper should be to give a very definite remedy for this type of pickling defect. Unfortunately the solution does not appear to be quite so simple. It has been stated that the magnitude of the pit is a function of time and current density, and any remedy that is applied must necessarily take these factors into account. The time referred to of course is pickling time, and any means of reducing pickling time will reduce the magnitude of the pit. The concentration and the temperature of the pickling acid may be subject to certain changes, which might bring about this effect. Possibly the use of tumbler tubs or agitation might be advisable. By such means pickle pitting of this type may be reduced to the point where it is no longer significant. The other variable that may yield to careful study is current density. The use of mechanical scale breaking has already been mentioned. The ratio of cleaned to scaled areas is greatly increased by this means, and the current density is correspondingly reduced. Since this action is a function of time and current density, this may point out the remedy. There are other means which might be mentioned which are not exactly true remedies, but rather means of avoiding this condition; sand blasting, for instance, as a substitute for pickling. The use of protective atmospheres will eliminate scale.

In reply to Dr. Speller, we are very glad to have his confirmatory results. We were familiar with the methods that he had developed to remove the first rolling scale, but we were not at the time aware that it was because of the potentials of the scale formed at higher temperatures.

In reply to Mr. Voorhees, the solubility of the scale itself, I believe, is still a controversial matter. Alloy scales, of course, are hard to remove. Possibly the composition of the inner layer between the metal and the oxide may be one of the most important factors in pickling. Of course if the surface of the scale happens to be hard and dense as is the case with some alloy steels, and the acid penetration is slow, the pickling time will be long. It is quite likely that Mr. Voorhees has observed some increased pitting at a time when there has been a change in the steel type—that is not at all uncommon.

In reply to Mr. Christin, we are sorry that we were not able to include the chromium-vanadium steels in this investigation. However, we were forced to limit the number of steels that we investigated. It is interesting to hear that they have observed more severe pitting with the chromium-vanadium types than with other steel types. Undoubtedly a study of the electrolytic potentials of chromium-vanadium steels through their heat treating range will show some very interesting figures.

Regarding Mr. Christin's remarks concerning the use of fresh acid and his observations that this effect had been noted more frequently when the acid was not fresh, there has been a general opinion for some years that pickling acids which are nearly spent are more liable to yield pitted surfaces than fresh acids. It is well known that spent acids do not pickle at as satisfactory a rate as fresh acids. The pickling time is increased, and consequently the pitting effect is increased.

DAMPING CAPACITY, A FACTOR IN FATIGUE

By G. R. Brophy

Abstract

The damping characteristics and endurance properties of several steels in several conditions of heat treatment have been determined and an attempt made to correlate these properties.

Damping capacity seems to be related to the damage resulting to steel from overstress and notches. High damping steels are resistant to sharp notches, but not to overstress, while low damping steels are resistant to overstress, but sensitive to notches. A limiting damping capacity, varying, it is believed, for different notches, is recognized. Below this limit, extreme notch sensitivity occurs.

Several factors influencing these properties have been studied and among the most important are grain-size and structure.

THE dependence of the endurance properties of metals upon their damping capacities has been referred to frequently in the past few years, but attempts at correlating these properties have been unsuccessful, except for a single steel, where it has been shown that, as the damping capacity is increased or decreased by thermal treatment, the opposite effect is noted on the endurance limit.[1] Canfield,[2] although believing that there is a relation, was unable to show it, or predict from his experiments, the endurance limits of steel.

Fatigue failure is reported to be the result of the accumulation of the damping effect,[3] or in other words, as a result of the fact that at a constantly repeated stress above the endurance limit damping increases at an increasing rate until fracture results. At a cyclic stress below the endurance limit damping either attains a constant

[1]G. R. Brophy, "Damping Capacity of Steels and Correlation with Other Properties," *Iron Age*, November 24, 1932, p. 800.

[2]R. H. Canfield, "Internal Friction in Iron and Iron Alloys," Transactions, American Society for Steel Treating, Vol. 20, 1932, p. 573.

[3]Pierre Chevenard, "The Mechanical Properties of Metals at Elevated Temperatures," Symposium on Effect of Temperature on the Properties of Metals, American Society for Testing Materials, June 1931, p. 155.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The author, Gerald R. Brophy, is metallurgist associated with the Research Laboratory, General Electric Co., Schenectady, New York. Manuscript received June 5, 1935.

value or continually decreases.[4] It is probably this changing value of damping which prevents an exact correlation.

In the presence of stress concentrations, damping lends appreciable protection as shown by the work at the Woehler Institute, and of others. It might be expected, too, that damping influences the resistance of metals to damage by overstress in the absence of notches.

Various factors controlling the damping capacity of steel have been studied,[2] but essentially composition and structure are most important. Grain-size, previously unrecognized among the structural differences, has been found of prime importance, even to the extent of masking or actually overcoming the influence of hardness.

The scope of the present paper includes a study of the influence of grain-size on damping capacity, and of damping on the damage resulting to steel in fatigue from notches and overstress.

Several steels were studied in various conditions of heat treatment, and were tested for damping capacity and endurance properties. All heat treatment was carried out on bars either 1 or 1⅛ inch diameter and test bars machined after heat treatment.

Damping capacities were measured on a Foepple-Pertz machine in which a vertical bar is set in free torsional vibration. By means of a stylus, a trace is obtained of the decaying vibration from which the decrement may be measured accurately. The specific damping capacity,[5] which is twice the logarithmic decrement, $P = 2\delta$ is plotted against the corresponding maximum shearing stress in torsion during the vibration decay. This damping capacity, of course, represents an average value over the entire volume of the bar.

The endurance properties were obtained from cantilever bars tested in a machine of our own design and construction, previously described.[6] The endurance limits are based upon 10,000,000 repetitions of stress. Both notched and unnotched bars were tested. The notch used was 0.035 inch deep and of 45-degree included angle and with but 0.0004 inch radius at the root. Stresses were calculated for notched bars on the net section at the base of the notch, using the ordinary bending formula and assuming no stress concentration. Special precautions were used to duplicate notches and minimize cold working as a result of machining. It is believed, too, that the influ-

[4]H. F. Moore and J. B. Kommers, "The Fatigue of Metals," McGraw-Hill Book Company, Inc., New York City.

[5]G. S. Von Heydekampf, "Damping Capacity of Materials," *Proceedings*, American Society for Testing Materials, Vol. 31, 1931, Part II, p. 166.

[6]T. S. Fuller, "Endurance Properties of Steel in Steam," American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930, p. 280.

ence of cold work is decreased by the use of deep rather than shallow notches.

Damping Capacity

In Figs. 1 to 3 are shown the damping characteristics of three steels of widely different compositions, each in three conditions of

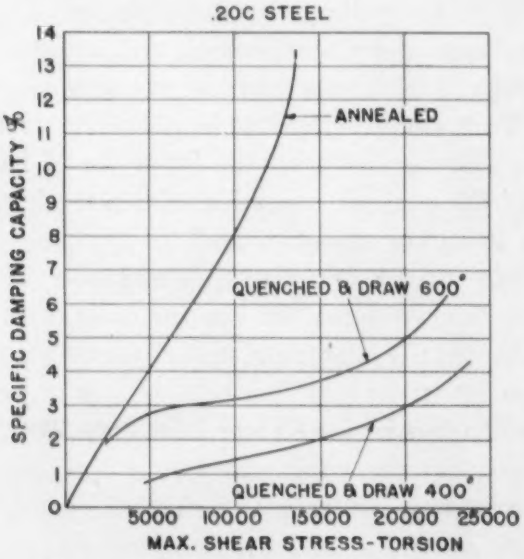


Fig. 1—Specific Damping Capacity Curves for 0.20 Per Cent Carbon Steel. Determined from Free Torsional Vibration.

heat treatment; annealed and after quenching from normal temperature and drawing from 400 and 600 degrees Cent. (750-1110 degrees Fahr.).

Fig. 1 shows the results for a 0.20-0.25 per cent carbon steel. In

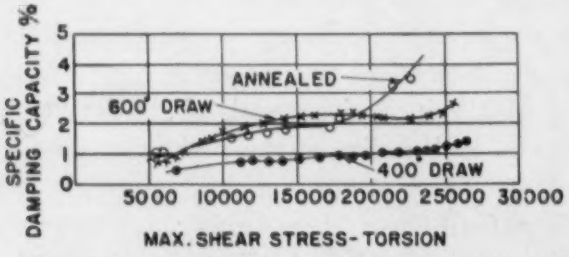


Fig. 2—Specific Damping Capacity Curves for 3½ Per Cent Nickel—0.36 Per Cent Carbon Steel. Determined from Free Torsional Vibration.

this case the two quenched samples show a marked reduction in damping with increase in hardness even though the hardness increase is but slight as compared to the other steels tested.

Fig. 2 shows the damping capacities for a 3.5 per cent nickel, 0.36 per cent carbon steel after normal annealing and normal quenching and drawing from 400 to 600 degrees Cent. (750-1110 degrees Fahr.). In this case, in spite of a relatively large change in hard-

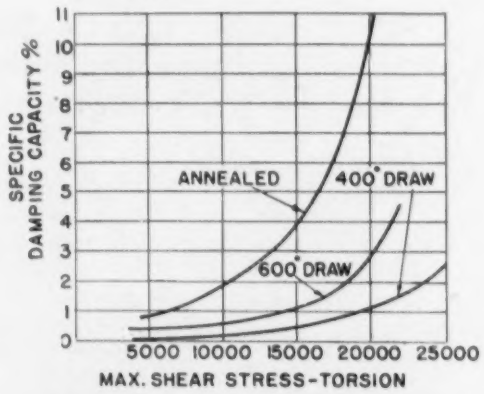


Fig. 3—Specific Damping Capacity Curves for 1.1 Per Cent Carbon Tool Steel. Determined from Free Torsional Vibration.

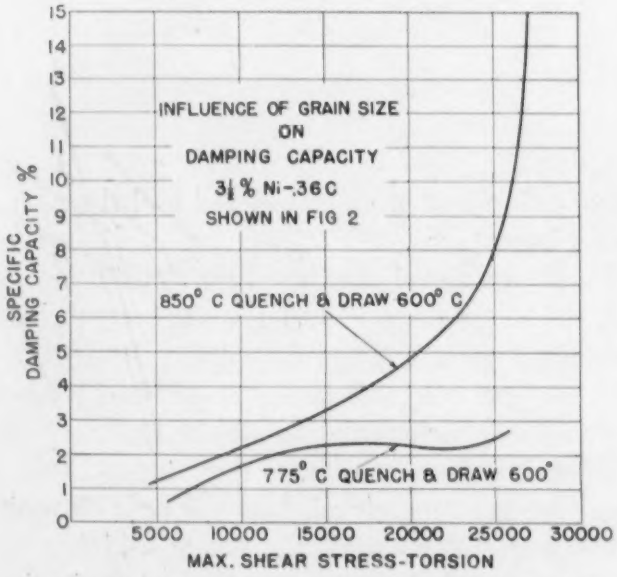

SPECIFIC DAMPING CAPACITY %
INFLUENCE OF GRAIN SIZE
ON
DAMPING CAPACITY
3½ % Ni-.36C
SHOWN IN FIG 2
850° C QUENCH & DRAW 600° C
775° C QUENCH & DRAW 600°
5000 10000 15000 20000 25000 30000
MAX. SHEAR STRESS-TORSION

Fig. 4—Influence of Grain-Size on the Specific Damping Capacity of the 3½ Per Cent Nickel—0.36 Per Cent Carbon Shown in Fig. 2.

ness, the damping values are only slightly different. The difference between the annealed and the quenched and 600 degrees Cent. (1110 degrees Fahr.) draw sample, in fact, is reversed at low stresses. As is to be expected, the 400 degrees Cent. (1750 degrees Fahr.) draw

which yields the hardest condition and produces the lowest damping.

A 1.1 per cent carbon tool steel shown in Fig. 3, because of its greater hardenability, shows lower results in the two quenched conditions.

In these three steels, the one which is not ordinarily considered a heat treating steel and which shows the least change in the usual physical properties, shows the greatest change in damping capacity. On the other hand the nickel steel which after these treatments shows

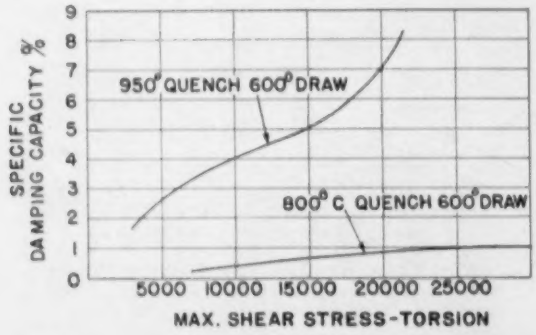


Fig. 5—Influence of Grain-Size on the Specific Damping Capacity of a 3.1 Per Cent Nickel—1.28 Per Cent Chromium—0.33 Per Cent Carbon Steel.

a considerable change in tensile properties shows the least. These results indicate an unrecognized structural influence as a possible controlling factor.

Grain-size differences were considered and the next experiments demonstrate its importance.

The 3.5 per cent nickel steel used previously was heated to 850 degrees Cent. (1560 degrees Fahr.) for one hour to develop a larger grain-size, and then quenched and drawn at 600 degrees Cent. (1110 degrees Fahr.). The damping characteristics are compared in Fig. 4 to those obtained after normal treatment. A marked increase is found, especially at higher stresses.

A steel of 3.1 per cent nickel, 1.28 per cent chromium and 0.33 per cent carbon was treated similarly, but at a higher temperature—950 degrees Cent. (1740 degrees Fahr.)—and again the damping is remarkably increased, but this time over all ranges of stress. Fig. 5.

This increase, it is felt, is due to the increased grain-size in spite of a possible tendency to increased hardness, which as has been shown,[1] tends to lower the damping capacity.

Since these comparisons were made on the basis of grain-size developed by heat treatment, it was of considerable interest to com-

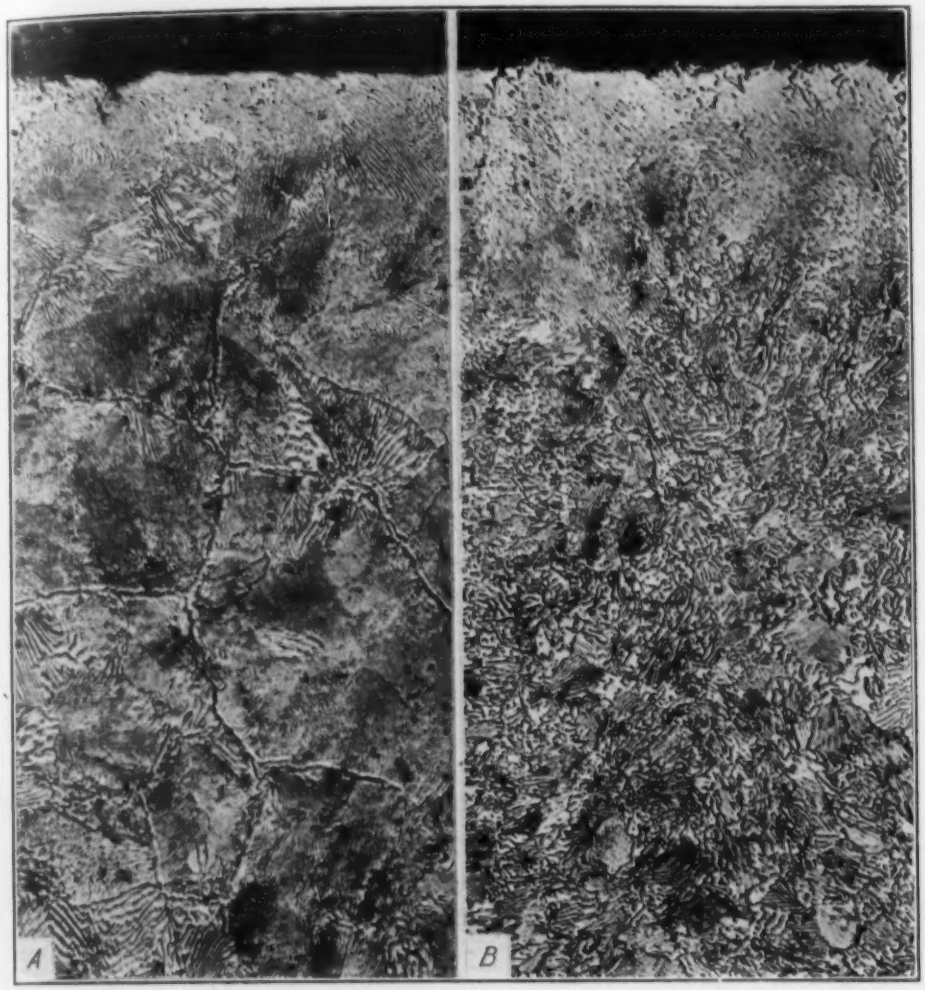


Fig. 6A—Inherently Coarse Grain Steel 0.37 Per Cent Carbon—0.71 Per Cent Manganese After McQuaid-Ehn Test. × 250. Fig. 6B—Inherently Fine Grain Steel of 0.36 Per Cent Carbon—0.62 Per Cent Manganese After McQuaid-Ehn Test. × 250.

pare two steels of like composition but of decidedly different inherent grain-size and normality. Accordingly, two steels were obtained, structures of which are shown in Fig. 6 after a McQuaid-Ehn test. The coarse-grained normal steel analyzed 0.37 per cent carbon and 0.71 per cent manganese while the fine-grained abnormal steel analyzed 0.36 per cent carbon and 0.62 per cent manganese.

These were heat treated normally from 820 degrees Cent. (1510 degrees Fahr.) and tested in the annealed and quenched and tempered conditions. The damping capacities are shown in Fig. 7.

Annealed, the damping capacities are high and not very different, but after quenching and drawing at 600 degrees Cent. (1110

degrees Fahr.), in which condition the inherent differences are emphasized, the damping capacity of the coarse-grained normal steel is considerably higher. The actual grain-sizes in the condition as tested, however, are not very different, as shown by the quenched and drawn structure in the upper halves of Figs. 8 and 9.

A further proof of the influence of grain-size on damping is provided by coarsening the grain of each of these steels. They were

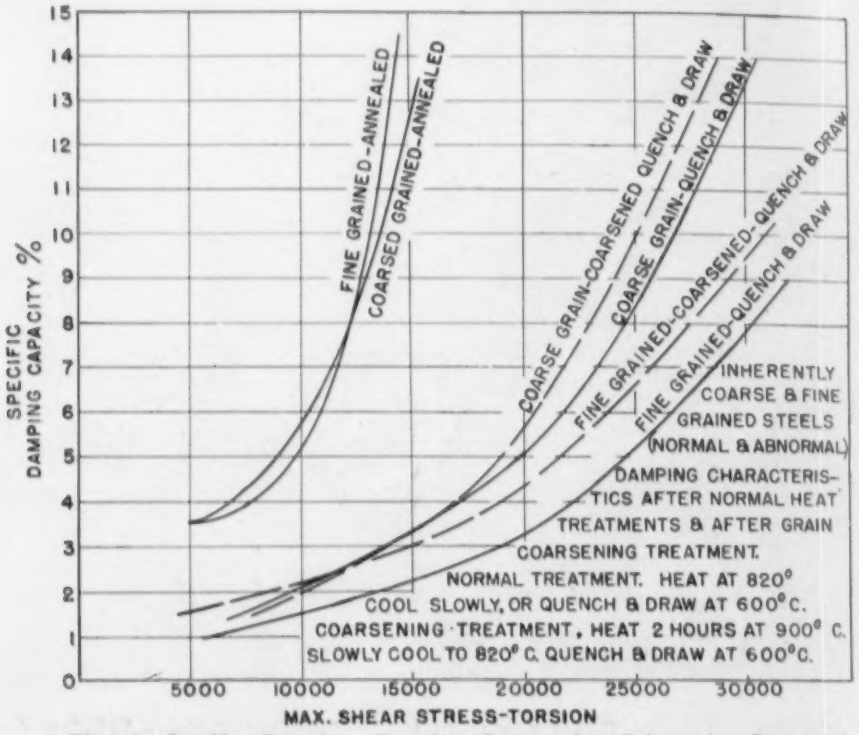

SPECIFIC DAMPING CAPACITY %
MAX. SHEAR STRESS-TORSION
FINE GRAINED-ANNEALED
COARSED GRAINED-ANNEALED
COARSE GRAIN-COARSENED QUENCH & DRAW
COARSE GRAIN-QUENCH & DRAW
FINE GRAINED-COARSENED-QUENCH & DRAW
FINE GRAINED-QUENCH & DRAW
INHERENTLY COARSE & FINE GRAINED STEELS (NORMAL & ABNORMAL)
DAMPING CHARACTERISTICS AFTER NORMAL HEAT TREATMENTS & AFTER GRAIN COARSENING TREATMENT.
NORMAL TREATMENT. HEAT AT 820° COOL SLOWLY, OR QUENCH & DRAW AT 600° C.
COARSENING TREATMENT, HEAT 2 HOURS AT 900° C. SLOWLY COOL TO 820° C. QUENCH & DRAW AT 600° C.

Fig. 7—Specific Damping Capacity Curves for Inherently Coarse-and Fine-Grained Steels in Normally Treated Condition and After a Grain Coarsening Treatment.

heated to a temperature of 950 degrees Cent. (1740 degrees Fahr.) for two hours; but, differing from the previous coarsening treatment used, were cooled slowly to 820 degrees Cent. (1510 degrees Fahr.), the normal quenching temperature, and then quenched and drawn at 600 degrees Cent. (1110 degrees Fahr.). The structures are shown in the lower halves of Figs. 8 and 9.

Each has had its damping capacity increased over the normal treatment by about the same amount (Fig. 7), but still the inherently fine-grained steel coarsened is lower than the normal for the inherently coarse-grained steel in spite of the enormous difference in actual grain-size.

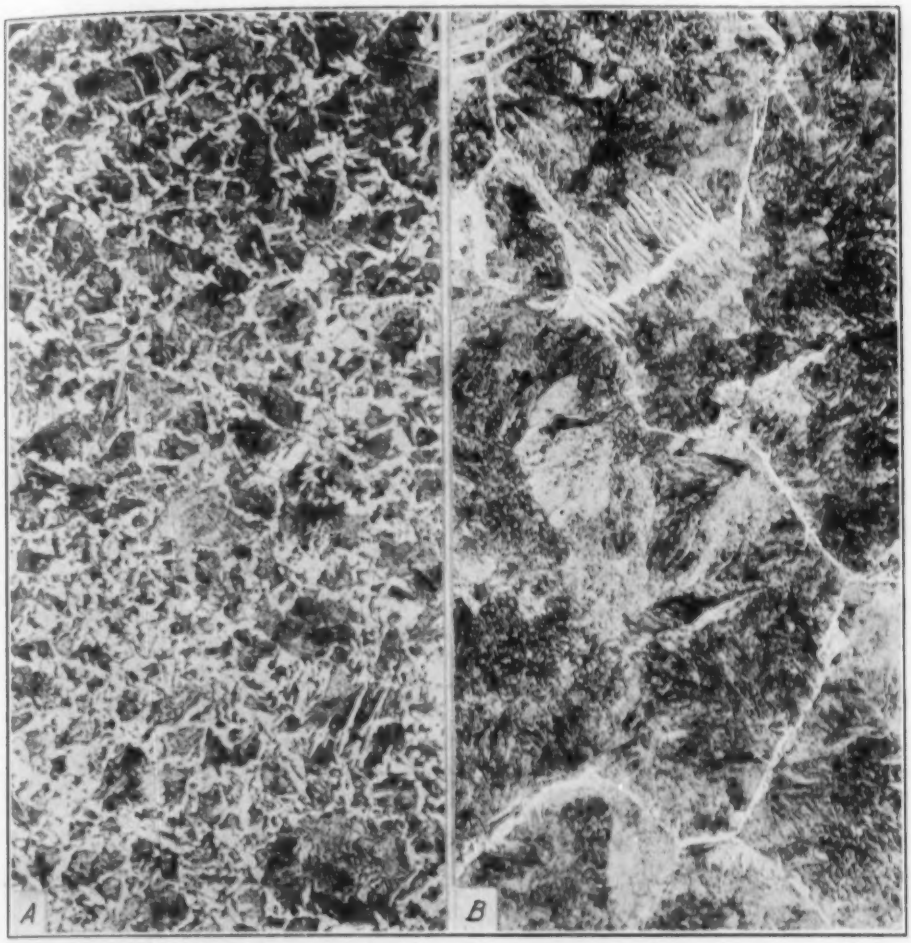


Fig. 8A—Inherently Coarse-Grained Steel as Tested After Normal Quench and Draw. × 250. Fig. 8B—After Grain Coarsening Treatment.

The Rockwell B hardness developed by these treatments is as follows:

Fine grain	—normal treatment	B 84.1
	—coarsened	B 92.3
Coarse grain	—normal treatment	B 86.5
	—coarsened	B 85.0

These results indicate again that grain-size is a controlling factor of greater importance than hardness, within limits. Still, the cause, whatever it may be, of differences in inherent grain-size apparently is of further importance but this may be, and probably is, a composition difference.

Another interesting difference in damping capacity is shown in

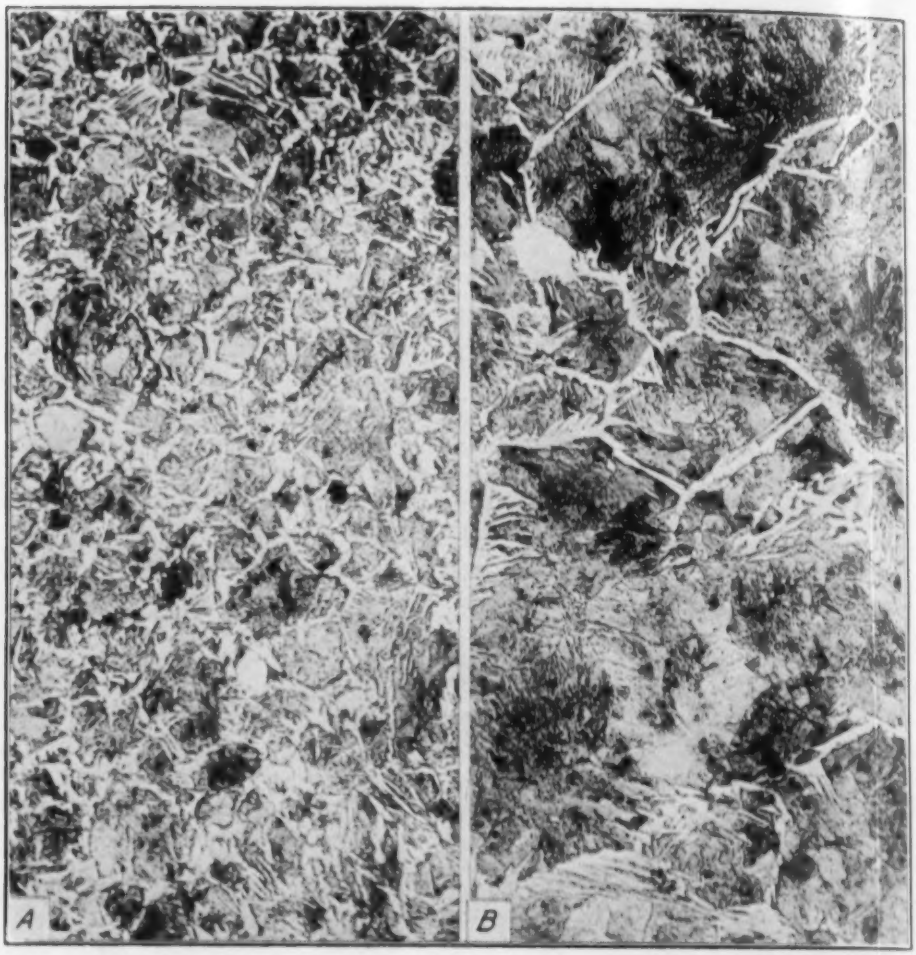


Fig. 9A—Inherently Fine-Grained Steel as Tested After Normal Quench and Draw. × 250. Fig. 9B—After Grain Coarsening Treatment.

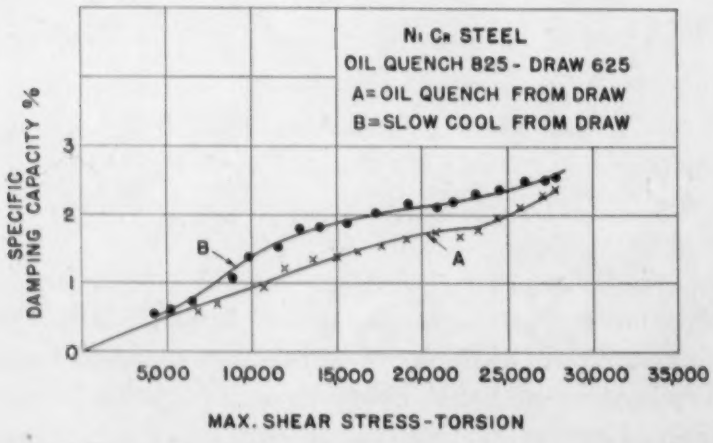


Fig. 10—Specific Damping Capacity of a 3 Per Cent Nickel —0.75 Per Cent Chromium—0.32 Per Cent Carbon Steel Oil Quenched from 825 Degrees Cent. and Drawn at 625 Degrees Cent. a—Quenched from the Draw. b—Furnace Cooled from the Draw.

Fig. 10. A nickel-chromium steel, different from that of Fig. 5, having a composition of 3.00 per cent nickel, 0.75 per cent chromium and 0.32 per cent carbon was quenched from 825 degrees Cent. (1515 degrees Fahr.) and drawn at 625 degrees Cent. (1160 degrees Fahr.). One set of bars was quenched from the draw and the other furnace

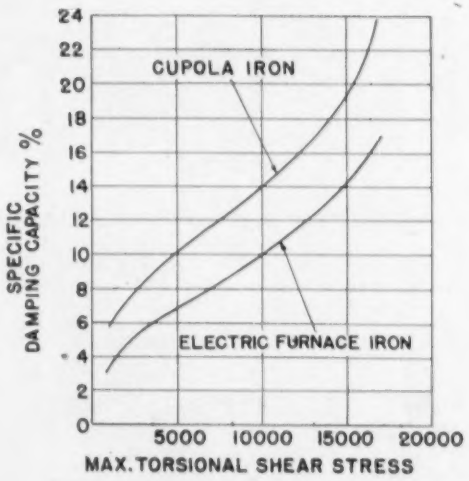


Fig. 11—Specific Damping Capacities of Two Gray Cast Irons of Similar Composition; One Made in the Cupola and the Other in an Electric Furnace.

cooled. The upper curve was obtained from the bar slowly cooled from the draw, and the lower for the bar quenched from the draw. While this difference is not great, it is apparently of some significance in connection with the endurance tests.

The influence of structure and composition is again emphasized by the damping capacities of two gray cast irons shown in Fig. 11. Iron No. 1 was melted in the cupola and No. 2 in an electric furnace. The compositions are as follows:

	No. 1 Per Cent	No. 2 Per Cent
Combined Carbon	0.61	0.68
Graphitic Carbon	2.66	2.48
Manganese	0.80	0.60
Silicon	2.05	2.26
Phosphorus	0.34	0.326
Sulphur	0.089	0.073

Endurance Tests

The stress-cycle curves for the first three steels tested are shown

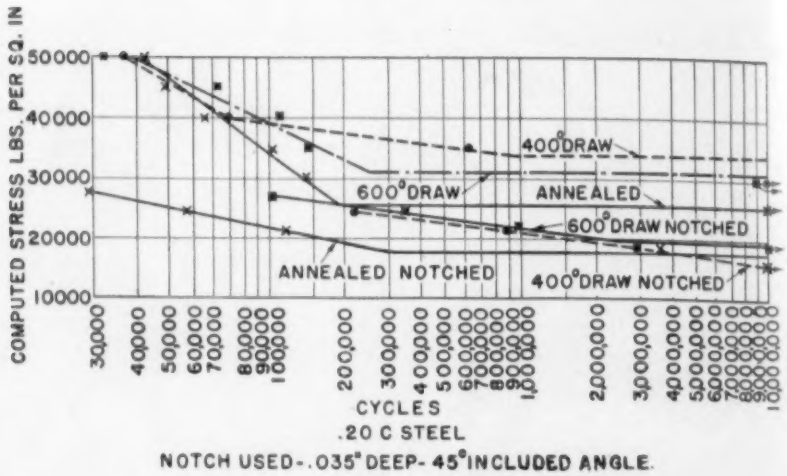


Fig. 12—Endurance Curves for the 0.20 Per Cent Carbon Steel (See Fig. 1). The Stress is the Extreme Fiber Stress in Pounds Per Sq. In. Computed by Means of the Bending Formula. In the Case of Notched Specimens the Stress is Computed as Before but on the Net Section at the Base of the Notch, Assuming No Stress Concentration.

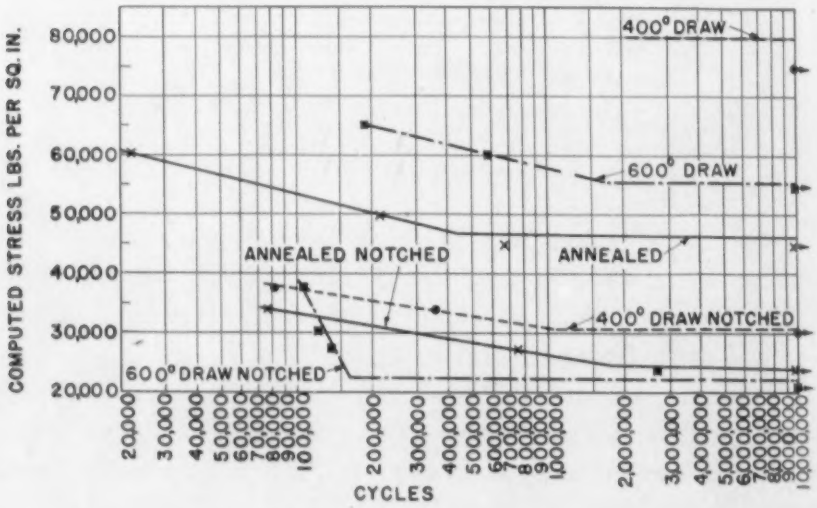


Fig. 13—Endurance Curves for 3½ Per Cent Nickel Steel, Damping Capacities of Which are Shown in Fig. 2. The Stress is the Extreme Fiber Stress in Pounds Per Sq. In. Computed by Means of the Bending Formula. In the Case of Notched Specimens the Stress is Computed as Before but on the Net Section at the Base of the Notch, Assuming No Stress Concentration.

in Figs. 12 to 14. The endurance limits for the plain bars fall in the order expected from the heat treatments given, and are of the magnitude expected from the probable tensile strengths developed.

In the presence of notches the endurance limits fall within a surprisingly narrow range of values, especially for any one steel, considering the range of tensile strengths which must have been

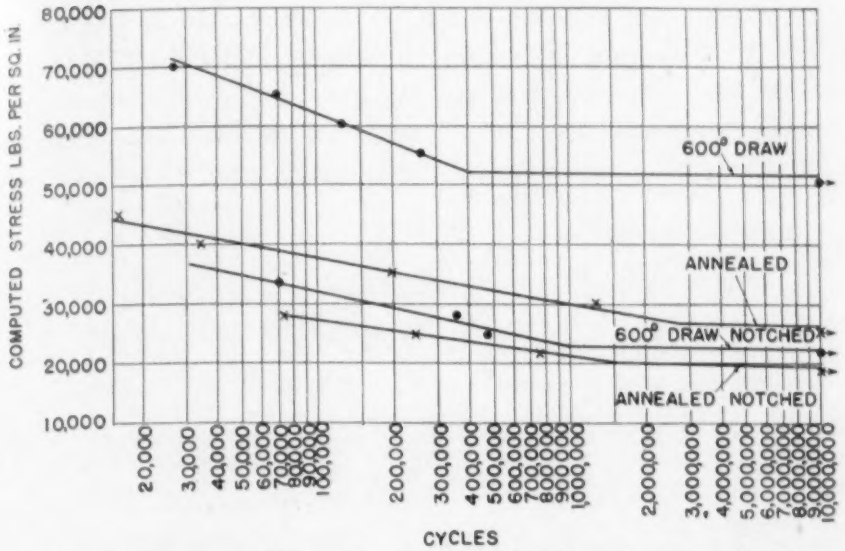


Fig. 14—Endurance Curves for 1.1 Per Cent Carbon Steel, Damping Capacities of Which are Shown in Fig. 3. The Stress is the Extreme Fiber Stress in Pounds Per Sq. In. Computed by Means of the Bending Formula.

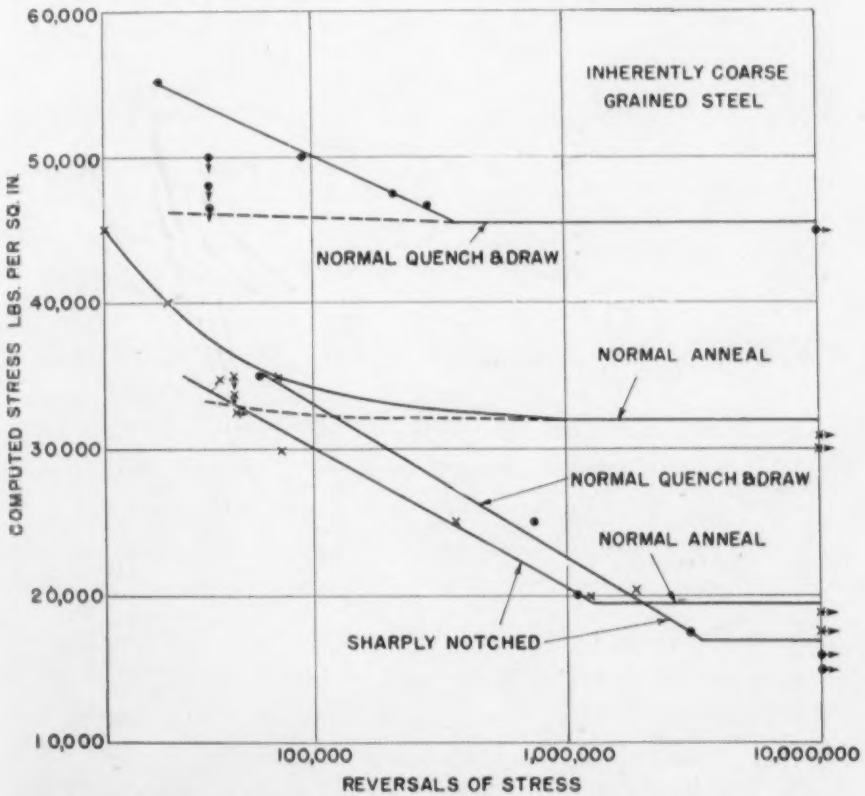


Fig. 15—Endurance Curves for Inherently Coarse Grain Steel After Normal Quench and Draw. See Fig. 7 for Damping Capacities. The Stress is the Extreme Fiber Stress in Pounds Per Square Inch Computed by Means of the Bending Formula.

developed, but no regular order is obtained. It is probable that notches of somewhat less severity would yield an order of values more like that obtained from smooth bars, and it was hoped that the sharp notches would definitely reverse the order. The strong tendency toward this condition, and the variation of the order, is further

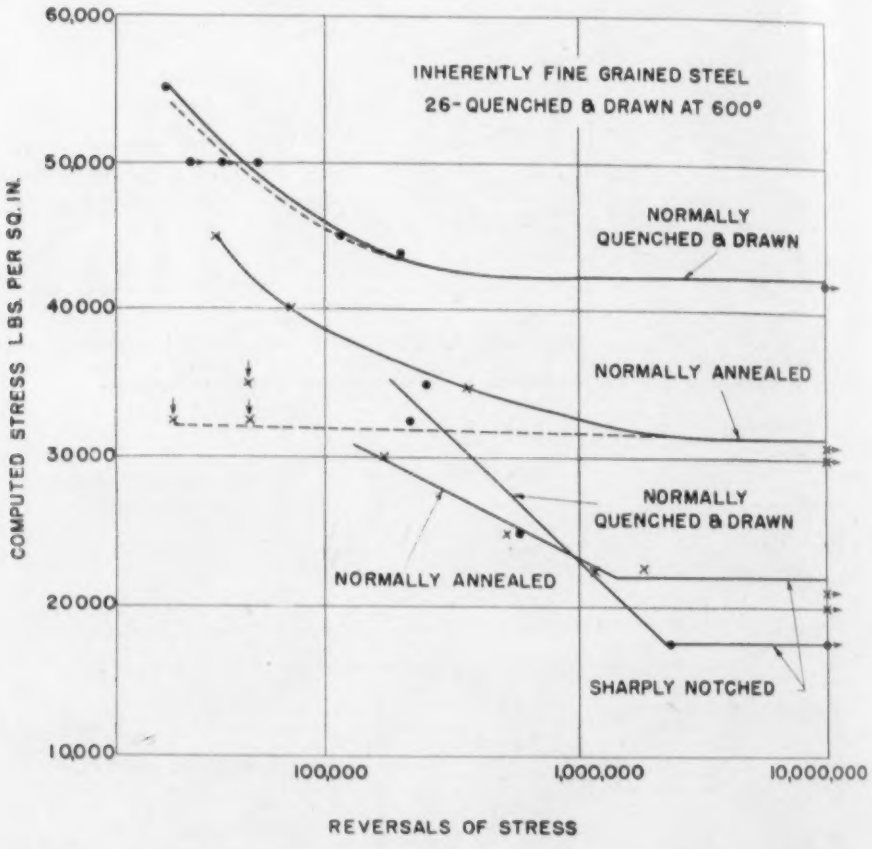


Fig. 16—Endurance Curves for Inherently Fine Grain Steel Normally Quenched and Drawn. See Fig. 7 for Damping Capacities. The Stress is the Extreme Fiber Stress in Pounds Per Square Inch Computed by Means of the Bending Formula. In the Case of Notched Specimens the Stress is Computed as Before but on the Net Section at the Base of the Notch, Assuming No Stress Concentration.

proof that the same values of stress concentration cannot be applied to all materials even though the geometrical conditions are the same.

In subsequent tests, the damage resulting from overstress was obtained also on smooth bars with some interesting results.

Fig. 15 shows the endurance limits both smooth and notched of the inherently coarse-grained plain carbon steel in the normally annealed and normally quenched and drawn conditions. To be com-

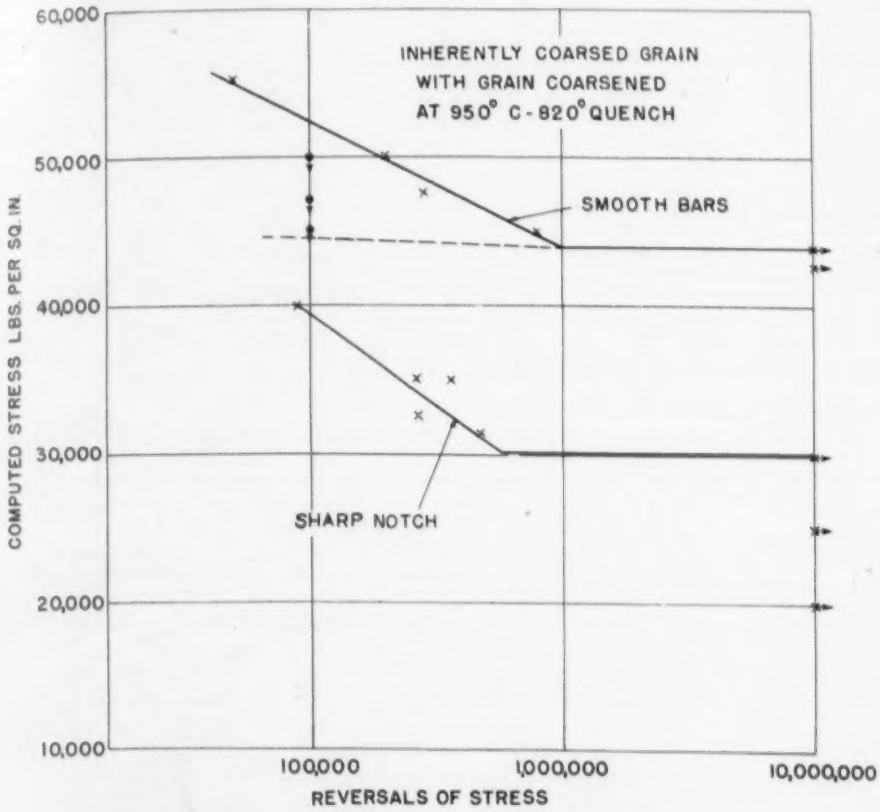


Fig. 17—Endurance Curves for Inherently Coarse Grain Steel After Grain Coarsening Treatment. See Fig. 7 for Damping Capacities. The Stress is the Extreme Fiber Stress in Pounds Per Square Inch Computed by Means of the Bending Formula. In the Case of Notched Specimens the Stress is Computed as Before but on the Net Section at the Base of the Notch, Assuming No Stress Concentration.

pared with these are the results from the inherently fine-grained steel tested under the same conditions. Fig. 16.

The smooth endurance limits for the two steels are not very different and the probable damage lines for the two annealed steels are both low. The large difference between these steels is exhibited after quenching and drawing. It is evident that the inherently fine-grained steel is not damaged by general overstressing, short of actual fracture, but the coarse-grained steel cannot be even slightly overstressed without damage.

In the presence of severe stress concentrations the annealed samples suffer a much smaller amount of damage than the quenched and tempered specimens, and show higher actual values. The stress concentration effect, as evidenced by the reduction of the notched endurance limit, is greater for the inherently coarse-grained material,

Table I

Steel	Treatment	Endurance Limits—Smooth	Endurance Limits—Notched	% Red. Due to Notch	Rockwell
Coarse Grained	Annealed 820°C.	32,000	19,500	42.5	
	Quenched 820 Drawn 600	45,500	17,000	62.6	B86.5
	950-820 Quenched Drawn 600	44,000	30,500	30.7	85.0
Fine Grained	Annealed 820°C.	31,500	22,000	30.6	....
	Quenched 820 Drawn 600	42,500	17,500	58.8	84.1
	950-820 Quenched Draw 600	42,000	26,000	38.0	92.3

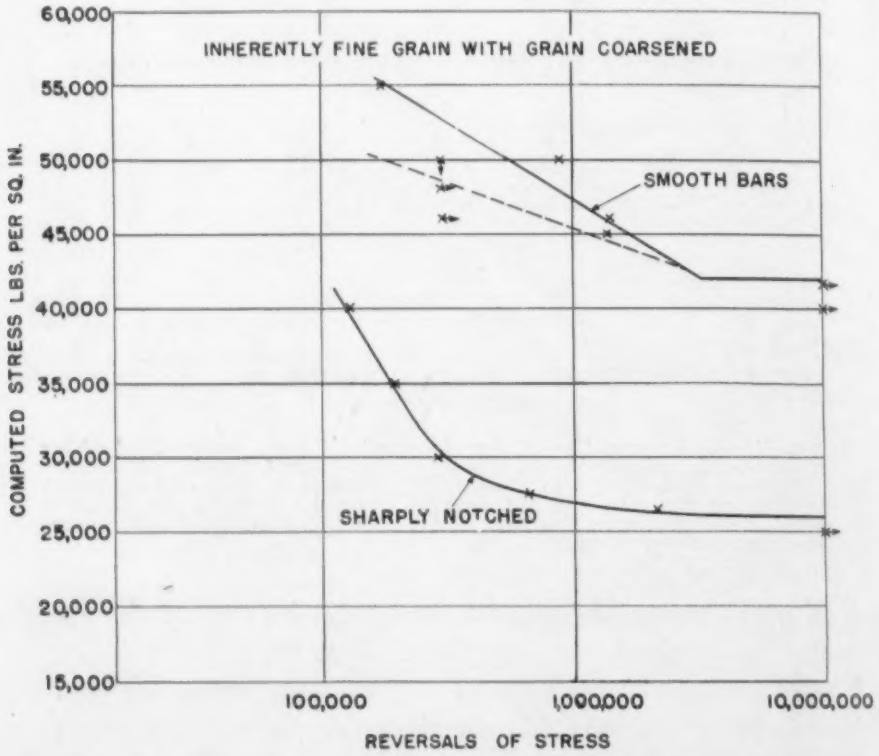


Fig. 18—Endurance Curves for Inherently Fine Grain Steel After Grain Coarsening Treatment. The Stress is the Extreme Fiber Stress in Pounds Per Square Inch Computed by Means of the Bending Formula. In the Case of Notched Specimens the Stress is Computed as Before But on the Net Section at the Base of the Notch, Assuming No Stress Concentration.

which in the condition tested has a somewhat smaller actual grain. See Figs. 8 and 9.

After the grain coarsening treatment previously described, the smooth endurance limits remain practically unchanged but the notched endurance limits show a marked increase in actual value and but approximately half the reduction. The probable damage

line of the inherently coarse-grain steel is not changed but is considerably lowered for the inherently fine-grained steel. Fig. 17 and 18.

These data are summarized in Table I.

The nickel-chromium steel, the damping capacities of which are shown in Fig. 10, was tested in smooth and sharply notched condi-

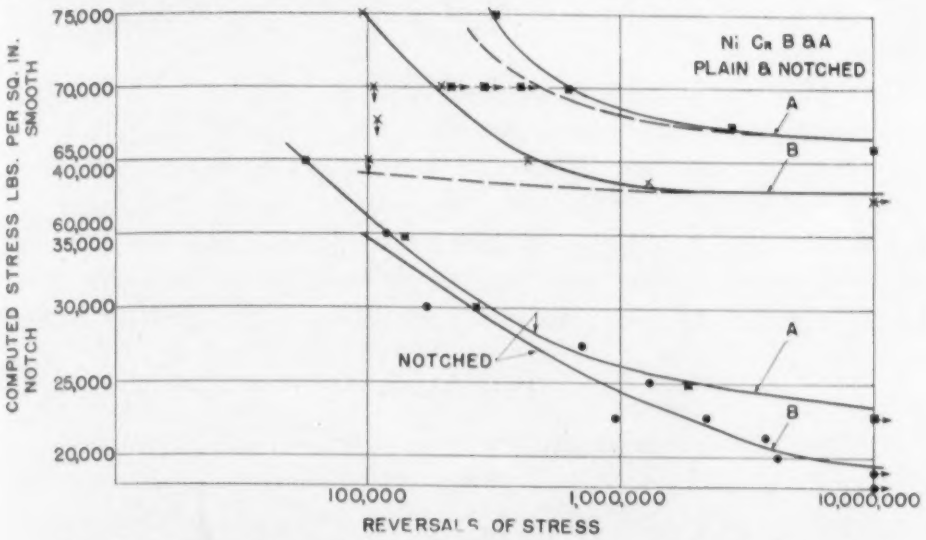


Fig. 19—Endurance Curves for Nickel Chromium Steel. A Quenched from Draw, and B Slowly Cooled from Draw. See Fig. 10 for Damping Capacities. The Stress is the Extreme Fiber Stress in Pounds Per Square Inch Computed by Means of the Bending Formula. In the Case of Notched Specimens the Stress is Computed as Before but on the Net Section at the Base of the Notch, Assuming No Stress Concentration.

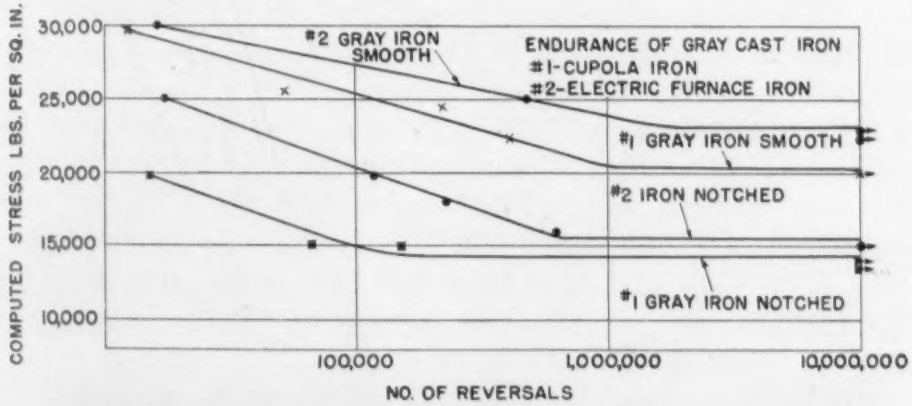


Fig. 20—Endurance Curves for Two Gray Irons. See Fig. 11 for Damping Capacities. The Stress is the Extreme Fiber Stress in Pounds Per Square Inch Computed by Means of the Bending Formula. In the Case of Notched Specimens the Stress is Computed as Before but on the Net Section at the Base of the Notch, Assuming No Stress Concentration.

tions. It should be remembered that this steel was quenched from 825 degrees Cent. (1515 degrees Fahr.) and drawn at 625 degrees

Cent. (1160 degrees Fahr.), one lot "A" was quenched from the draw and the second, lot "B", was furnace cooled. The tensile properties show practically no difference, but the Charpy value of lot A was 34.5 foot-pounds and that of lot B was 17.6 foot-pounds.

Fig. 19 gives a comparison of the endurance properties of both smooth and sharply notched bars. Lot A shows a higher smooth endurance limit than lot B and less susceptibility to damage by overstress.

While no definite notched endurance limits are found up to 10,000,000 cycles, the notch sensitivity is estimated to be approximately 65 per cent for the A specimens and 70 per cent for the B.

A comparison of the endurance limits for the two gray cast irons, Fig. 20, shows the electric iron to advantage, but its notch sensitivity is somewhat greater than that of the cupola iron. Both, however, are among the least notch sensitive of the materials studied.

Discussion

Since the damping capacities were determined in reversed torsion and the endurance limits in reversed flexure, it is necessary for purposes of correlation to compare them on the common ground of the maximum shear stress developed in each test.

From theoretical considerations, in the case of flexure, the maximum shear stress is one-half the maximum tension stress so that to have a comparison on the basis of maximum shear, it is required that the flexural endurance limit be expressed in terms of the maximum shear stress developed.

From actual fatigue tests,[7] however, made in both flexure and torsion, the ratio of the endurance limit for reversed torsion to the endurance limit in reversed flexure has been found to vary from 0.44 to 0.71 with an average value of 0.55 instead of the theoretical 0.50. This value of 0.55 is supported by averaging the data from Von Heydekampf's curves[5] of the damping capacities of several steels tested in torsion and flexure.

It is also necessary to pick some definite stress at which to determine the value of damping, since this property varies continuously with stress. There are two possibilities, both of which bring us to the same general conclusions, but with somewhat different actual values. The first is to use the damping capacities at shear stresses

[7] H. F. Moore and J. B. Kommers, "Fatigue of Metals," McGraw-Hill Book Co., Inc., New York City, p. 148.

equivalent to the nominal notched endurance limit and plot these against the stress concentration factors.* A second value of damping may be determined at the smooth endurance limit expressed in terms of maximum shear.

Using the factor 0.55, the nominal endurance limits smooth and notched have been recalculated to maximum shear stress, and the damping capacities at these stresses have been plotted against their respective stress concentration factors (or the percentage of reduc-

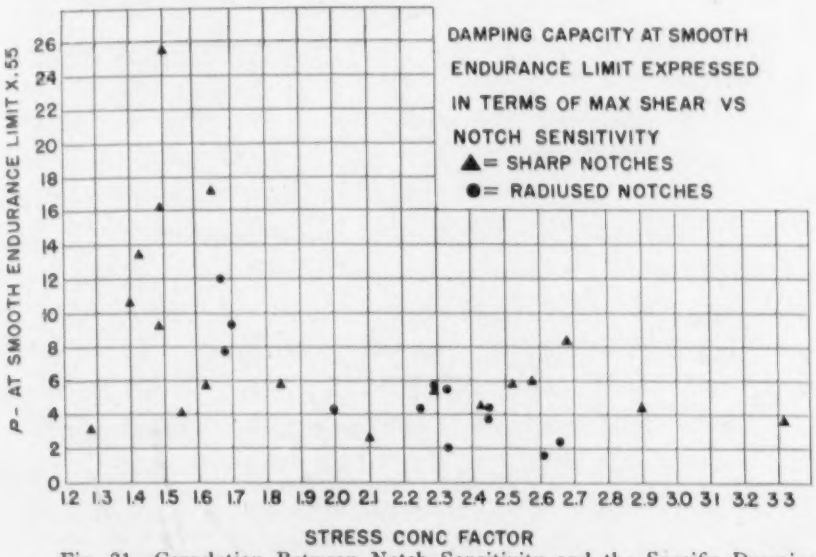


Fig. 21—Correlation Between Notch Sensitivity and the Specific Damping Capacity at the Maximum Shear Stress Corresponding to the Smooth Endurance Limit.

tion) with the diagrams resulting in Figs. 21 and 22. Data from additional tests, and represented by the circled spots, were obtained from several different steels, the notched fatigue bars of which had radii of 0.010 inch at the roots.

Considerable scatter is observed, but undoubtedly some of this is the result of using the factor 0.55, which is but an average value.

The correlation between the notch sensitivity and the damping capacity at the notched endurance limit expressed in terms of maximum shear seems to be better in that less scatter is obtained, although the same trend is noticed in both methods. There appears to be a limiting damping capacity for the notches used, below which, notch sensitivity assumes dangerous proportions, and above which, a considerable protection results.

*Note: Stress Concentration Factor $= \frac{\text{Smooth endurance limit}}{\text{Notched endurance limit}}$

That structural composition plays an important part in notch sensitivity is shown by the fact that the annealed plain carbon steels, having a considerable free ferrite content, and cast irons fall as a group well above the general trend of the curve, indicating a greater resistance to notch effects. On the other hand, the annealed 1.1 per cent carbon steel which contains a free carbide network is

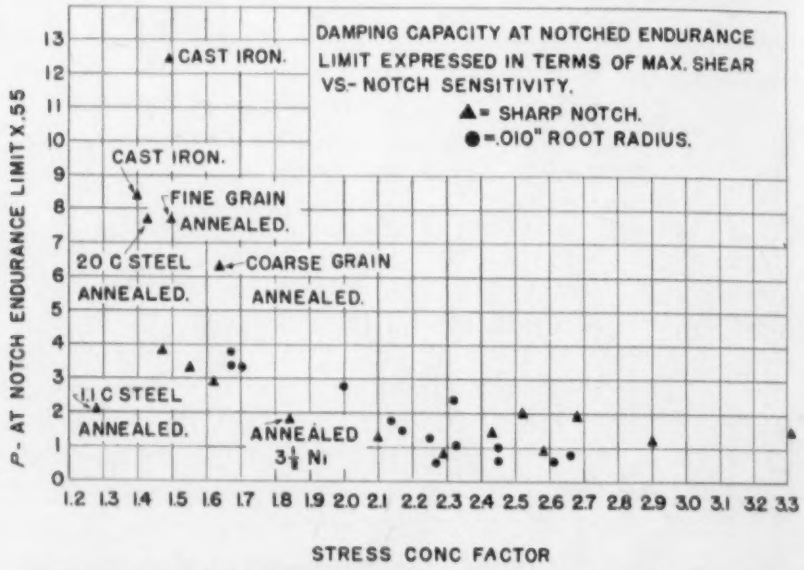

DAMPING CAPACITY AT NOTCHED ENDURANCE LIMIT EXPRESSED IN TERMS OF MAX. SHEAR VS- NOTCH SENSITIVITY.
▲= SHARP NOTCH.
●=.010" ROOT RADIUS.
CAST IRON.
CAST IRON.
FINE GRAIN ANNEALED.
2.0 C STEEL ANNEALED.
COARSE GRAIN ANNEALED.
1.1 C STEEL ANNEALED.
ANNEALED 3½ Ni
P- AT NOTCH ENDURANCE LIMIT X.55
0 1 2 3 4 5 6 7 8 9 10 11 12 13
1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3
STRESS CONC FACTOR

Fig. 22—Correlation Between Notch Sensitivity and the Specific Damping Capacity at the Maximum Shear Stress Corresponding to the Notched Endurance Limit.

an exception in that it has a low damping capacity as well as a low notch sensitivity.

Increasing the grain-size of any steel develops greater plasticity as indicated by a marked rise in damping capacity, Figs. 4, 5, and 7, and as a result the high stresses which are momentarily set up at a sharp notch are decreased, undoubtedly, by rapid change in the contour. At the same time, because of greater plasticity, the work hardenability of the metal is increased, thereby strengthening the metal immediately at the root. Support for this view is obtained from experiments with some austenitic steels which have great capacity for work hardening, a high measured damping capacity and a small, if any, notch sensitivity. As a matter of fact by enlarging the grain-size of such material, notched endurance limits using a sharp notch were obtained which were actually superior to those obtained on smooth bars. The notch concentration factor obtained was 0.745 with a damping capacity of 8.8 per cent at the notched endurance limit.

It seems paradoxical that steels which are able to withstand the extreme stresses set up at the root of a notch should be damaged to the extent they are by a general surface overstress of much lower intensity. It is believed that it is just this difference in intensity of stress which accounts for the two actions. The extreme stresses probably cause instantaneous strengthening in those plastic steels capable of a high degree of work hardening, i.e., high damping steels, whereas stresses of relatively low intensity produce work hardening and strengthening at disproportionately lower rates.

In practice, these differences have been noted frequently in the cold rolling of steel. For instance, heavy cold reductions of section result in a high rate of hardening and strengthening, while light passes for the same total deformation yield less hardening and permit of greater reductions of section between anneals.

Further confirmation of this hypothesis is obtained from the cold rolling of two high carbon steels[8] where it developed that an inherently coarse-grained steel, now known to have high damping capacity, work hardened to a considerably greater extent than a fine-grained steel for the same total deformation.

The superiority of coarse-grained steels in resisting notch effects in fatigue is not shown, however, when high stresses are suddenly applied, as in the impact test. Charpy tests of the inherently fine- and coarse-grained steels show in their normally quenched and tempered states impact values of 44 foot-pounds, but when the grain is abnormally coarsened the values drop to 7 to 12 foot-pounds.

From the fact that some steels show great resistance to damage by general overstress, and others low resistance, the question as to how rapidly a material fails in fatigue seems to be answered. The rate of failure varies from one material to another and depends fundamentally upon damping capacity. A steel having a low damping capacity which is associated usually with high strength and small grain-size resulting from quenching and tempering shows great resistance to the start of a crack, but once started complete failure is sudden because of its high notch sensitivity. Conversely, a steel of high damping capacity probably starts a surface crack after relatively few cycles of stress but because of its low notch sensitivity failure progresses slowly.

A study of the endurance properties of steels at very high

[8]G. R. Brophy and L. L. Wyman, "Factors Influencing the Annealing of Cold Rolled Strip Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 21, 1933, p. 535-6.

stresses, so that life is short, and particularly the determination of the true damage line at these stresses, should be of great interest. It is improbable that the conditions relating to overstress, as represented in the stress-cycle diagrams of this paper, continue on to high stresses. It is likely that the probable damage line bends upward, more or less paralleling the fatigue line some distance, then it bends toward the stress axis and joins the fatigue line close to, or at, the axis. Thus a damage area is bounded by the endurance curve and the damage line. This area should vary with the kind of material and its heat treatment, and from indications obtained from preliminary experiments, its damping capacity. It is suggested, too, that stressing up to the damage line may result in actual strengthening.

DISCUSSION

Written Discussion: By T. McLean Jasper, A. O. Smith Corp., Milwaukee.

The correlation between damping effect and fundamental endurance limits, it is believed, is going to be difficult, because at the endurance limits of steels the elastic limits are very rarely exceeded. When they are exceeded, such elastic limits are relatively very low as compared to the ultimate strength.

The writer, if the interpretation he has placed on the meaning of Mr. Brophy's paper is correct, is of the opinion, that the damping capacity probably allows a steel to be selected which is to a greater or lesser degree sensitive to notch effect. The fundamental endurance of steels in the absence of stress raisers is fairly well correlated to tensile strength. The notch sensitivity of such steels, however, may be measured by endurance tests with notched specimens when properly correlated with the fundamental endurance limits, or possibly by a proper interpretation of "damping capacity."

Many metallurgists, and some engineers, are inclined to measure notch sensitivity by the use of the transverse notched bar impact specimen. We have the results of a very extensive investigation by Almen and Boegehold[1], in which this point of view is rendered to a large degree untenable, or may it be said, less tenable than sometimes supposed. A careful study of the paper by Almen and Boegehold disclosed the fact, that the notched bar impact test does not correlate with the usefulness of steels, as applied to automobile rear axle gears. A very extensive paper before the North East Coast Institution of Engineers and Shipbuilders by MacGregor, Burns and Bacon[2], confirms this general thesis on propeller shafting.

If, therefore, the damping capacity tests can be utilized in conjunction with fatigue to establish a measure for the illusive property of notch sensitivity of steels to be used in machine parts, then it is believed that Mr. Brophy's paper is a fundamental contribution to materials testing.

[1] J. O. Almen and A. L. Boegehold, "Rear Axle Gears, Factors which Influence their Life," American Society for Testing Materials, 1935 Preprint No. 27.

[2] *Transactions*, North East Coast Institution of Engineers and Shipbuilders, Vol. LI, 1935.

In discussing this paper with reference to grain-size, a careful study of the Almen and Boegehold paper discloses the fact that grain-size and notch sensitivity as measured by fatigue results may not correlate as nicely as seems to be desired. It is possible, that steels that are notch sensitive, are also associated with more discontinuations than steels not so notch sensitive. If this is true, it is believed that no amount of heat treatment can be expected to heal up these discontinuations. It is possible that the result of reduction of grain-size has been to present a more tedious path for fracture to traverse, and in this manner lengthen the time for fracture to disclose itself.

The writer is not unmindful of the fact that strengthening heat treatments tend to increase the endurance limits when using the smooth specimen. It has also been demonstrated that sometimes when a notch is introduced into a specimen or machine part, the effect of this increase in strength by heat treatment has been to lower the notch endurance limit or service values of the steel.

It is believed that repeated stress tests on notched specimens is the nearest approach to the service requirements for certain parts of machinery which a testing laboratory can furnish. Such tests to select the most appropriate steels for designs are tedious to perform, and if some more rapid method can be devised, let us at least use it to eliminate the most undesirable steels. The close selection as between a few steels can be carried out by the more tedious test methods. The final selection will always be left to the service record of equipment.

Written Discussion: By H. F. Moore, Research Professor of Engineering Materials, University of Illinois, Urbana, Illinois.

Mr. Brophy's paper is a most interesting study of the correlation of damping capacity, notch sensitivity and fatigue strength of metals. One factor which may prove of importance in this, and in other studies of notch sensitivity is the report by R. E. Peterson of the Westinghouse Electric and Manufacturing Co.[a] that a rather soft steel tested by him showed low notch sensitivity for small specimens, but distinctly higher notch sensitivity for large specimens. This factor of size effect may need investigation in connection with the correlation of notch effect and damping capacity.

The apparent effect of increasing damping capacity as grain-size increases may, perhaps, be explained by the relatively large amount of hysteresis developed in an overstressed large grain, and by the relatively small area of boundary material between grains in large-grain metal, with a consequent reduction of resistance to spread of plastic action from one grain to another.

Fig. 1 of this discussion shows micrographs of fatigue cracks in two metals: (1) a soft structural steel which would presumably show high damping properties and low sensitivity to notch effects, and (2) a heat treated nickel steel which would presumably show low damping properties and high notch sensitivity. It will be noted that in the soft structural steel a fairly wide strip on either side of the crack shows slip lines. Evidently appreciable slip has taken place to a depth of four or five grains on either side of the crack. In contrast, there seems to be a very small width of metal disturbed by slip in the heat treated nickel steel.

[a] At the meeting of the Applied Mechanics Section of the American Society of Mechanical Engineers at Ann Arbor, June 1935.

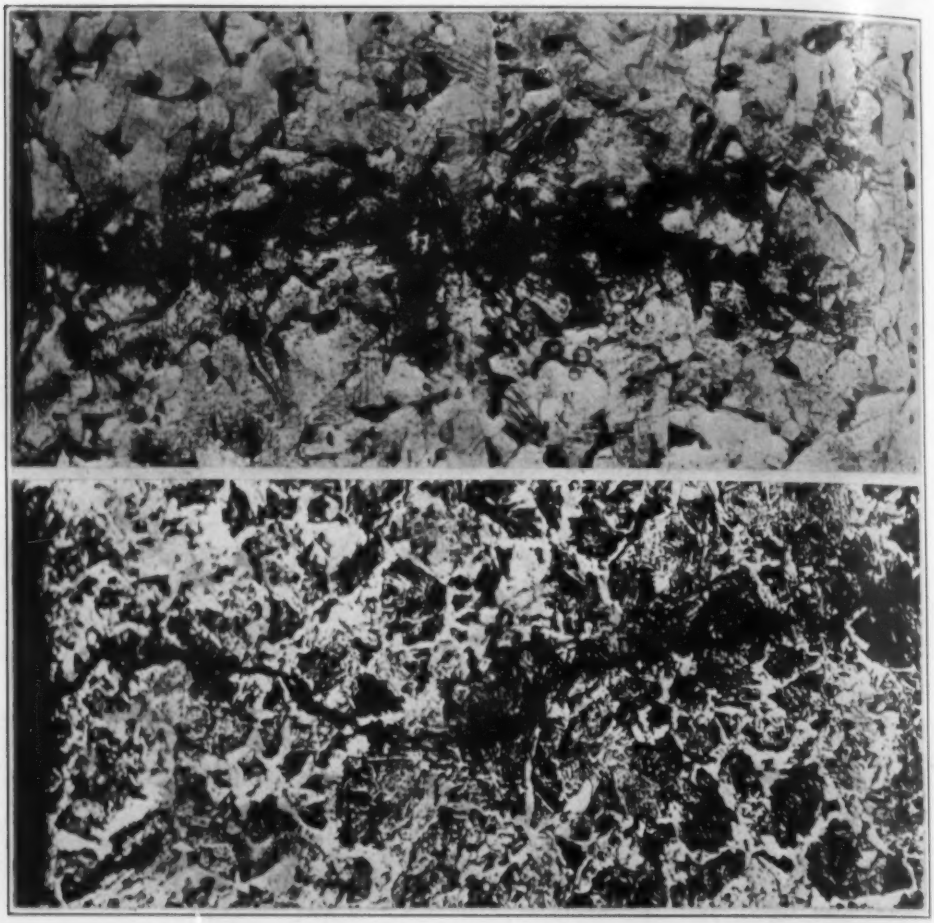


Fig. 1—Micrographs of Fatigue Crack in Structural Steel (upper) and Heat-Treated Nickel Steel (lower). Magnification, 200 Times. Micrographs by R. E. Cramer.

It would appear that in the structural steel a considerable amount of energy is absorbed in slip in the grains—energy which otherwise would be available for forming a crack. In the heat treated alloy steel any energy above the elastic energy of deformation has little outlet in disturbing areas by slip and is more likely to start a crack. Of course, it must be remembered that the heat treated nickel steel can develop more elastic energy than the soft steel.

In the case of a notched piece of steel, either structural steel or heat treated alloy steel, there would in nearly all cases be some plastic action at the root of the notch, but the energy which could be absorbed in crackless slip over the relatively large "disturbed" area of the structural steel would be in excess of that which could be cracklessly absorbed in the small disturbed area of the heat treated nickel steel.

In Fig. 2 is shown the damage lines that were obtained in the Fatigue of Metals Laboratory of the University of Illinois for rail steel and for cold drawn screw stock. In the figure for rail steel points *a*, *b*, *c* and *d* represent the number of cycles and the magnitude of stress applied to four "overstressed" specimens while

points *t*, *u*, *v*, *w*, *x*, *y* and *z* represent the points determined for the stress-strain diagram of the virgin metal. After overstressing, each of the specimens *a*, *b*, *c*, and *d* were put in a testing machine and tested either to fracture or to 10,000,000 cycles under a reversed stress of 63,000 pounds per square inch—the endurance limit of the virgin metal. Specimens *a*, *b*, and *c* "ran out" without

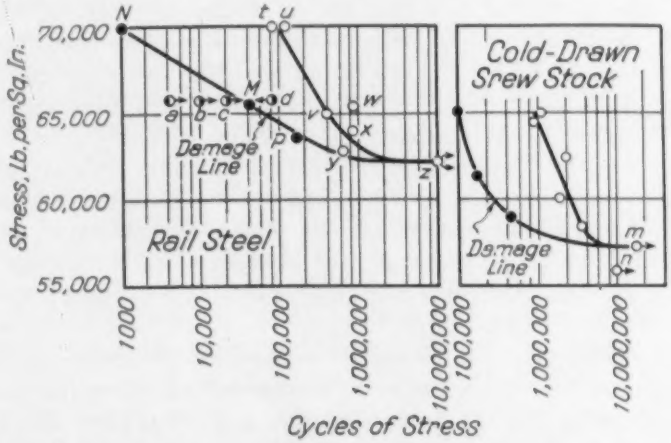


Fig. 2—Damage Diagrams for Rail Steel and Cold-Drawn Screw Stock.

fracture, specimen *d* fractured. The point *M* located between *c* and *d* is taken as a point on the damage line. Points *N* and *P* were determined in similar fashion, and the damage line drawn through them, thus locating the approximate limit of cyclic stressing at any given stress which the material can withstand without reduction of its virgin endurance limit.

It will be noted in Fig. 2 that for the cold drawn steel there is some tendency shown for the "closing" of the damaged area at the high stress. More tedious experimentation must be made before this tendency can be verified.

Mr. Brophy notes that the low damping steels he tested were resistant to overstress, while the high damping steels were not. For notch sensitivity he noted that the order of merit of the two types of steel was reversed. This seems to indicate that there is a marked difference between the failure of a notched fatigue specimen and an unnotched specimen. It is suggested that in the case of a notched specimen the opportunity for the distribution of slip is limited, and that the damaged area which occurs around weak or unfavorably oriented grains may be regarded as a specimen with a short gage length, in which little total elongation (in inches, mm, or microns) is necessary to produce a large *percentage* elongation—a sufficient percentage elongation to start a spreading tensile (or shearing) failure. In the case of an unnotched specimen the damaged area is not confined by the walls of a sharp notch, and the "gage length" is greater. In the case of the notched specimen slip in one "unfortunate" grain would then be more likely to start a spreading crack than would be the case with an unnotched specimen.

In connection with the author's remarks concerning the rate of speed of damage in various steels, it would seem that a study of speed effect of fatigue testing might be of interest. Testing machines of the rotating beam type operating at as high as 10,000 cycles per minute are now on the market and

fatigue and "damage line" tests on plain and notched specimens at various speeds would seem a profitable line of study.

It is to be hoped that this paper with its valuable results will stir up a number of experimentors to follow the lines of work Mr. Brophy has suggested. Perhaps this may be the line of attack which will answer that puzzling question, "when and under what conditions do cycles of repeated stress cease strengthening metal by cold work and begin to weaken it by a spreading crack?"

Written Discussion: By J. Fletcher Harper, Allis Chalmers Manufacturing Co., East Allis, Wisconsin.

In reference to this paper there are several questions and comments which I would like to advance. In regard to the two carbon steels of like composition but of different inherent grain-size, how did these steels obtain their inherent grain? Was a fine grain secured in the melting by the use of aluminum? And if so, was not certain of the effects due to the finely dispersed alumina?

It was assumed that the chemical composition being approximately the same, that the same heat treatment as to temperatures of annealing and quenching should produce similar results on structure and properties. We have found that this is not true in the treatment of coarse- and fine-grained steels and that the fine-grained material has a wider treating range to secure equivalent results. It would appear that if the coarse-grained material had been treated at the optimum temperature (which is undoubtedly lower) for annealing and quenching the damping and endurance properties of the inherently coarse-grained and fine-grained material would be in close agreement.

In support of this, the specific damping capacity of the coarse-grained steel, coarsened, is increased less over the coarse-grained steel than the fine-grained steel, coarsened, over the fine-grained steel.

The comparison of the two steels and the two cast irons of similar analysis but different melting methods to show the effect of grain-size, is of interest. However, lacking photomicrographs of the cast iron, it can be assumed that the difference in the iron is in the graphitic flake which can only be altered by remelting; while in the steel, we believe that by suitable heat treating temperatures the coarse-grained material can be made to closely approach the fine-grained steel.

In the endurance properties of the smooth bars of the fine-grained and coarse-grained steels, the greatest variation is in the damage lines of the quenched and drawn material. It is our belief that the damaging by overstressing of the coarse-grained steel can be greatly reduced and made to approach, if not equal, the fine-grained material, by the use of the optimum temperature to actually secure the same grain structure as the fine-grained material.

In the coarsened material (Figs. 17 and 18), the damage line is considerably lowered for the inherently fine-grained steel, while not materially changed for the inherently coarse-grained material. This, we believe, shows the coarse-grained material has probably reached the maximum effect (due to coarsening) on the damage line in the so-called normal condition, while the fine-grained material, if treated at higher temperature (or longer time), could still

have the damage line lowered before the grain-size would effect the endurance limit.

It must not be construed that we recommend coarse-grained steel, but we believe that many coarse-grained steels (subject to certain melting conditions, etc.) can be made equal to fine-grained steels of the same composition by a proper narrow heat treating range which is different from that for fine-grained steel. In many cases this refinement of treatment is not economical.

In regard to the nickel-chromium steel quenched from the tempering temperature and furnace cooled from the tempering temperature, I would like to inquire as to the tempering times.

If the tempering time of (Curve A, Figs 10-19) the quenched material was not prolonged over (Curve B, Figs. 10-19), the material slowly cooled, the effective tempering heat would be greater in the latter material, and the endurance limit could well be less.

The quenching from the tempering heat can be considered as retaining a solid solution (probably in the ferritic constituent) by the rapid cooling, while in the slowly cooled material an age hardening effect takes place by the formation of a shower of particles of solute metal or compounds. It would be interesting to reheat the material treatment "A" to some lower temperature to see if this material did not age harden.

Written Discussion: By O. J. Horger, Ann Arbor, Michigan.

The author does not state in his paper whether or not the damping curves for the various steels were obtained after the specimens had been subjected to a cyclic stress. It has been shown by other investigators[1] that the damping characteristics for a material do not become stable until it has been subjected to several million cycles of stress reversal. Therefore if the author made his damping tests previous to cyclic stressing the material, his damping curves involve both elastic and plastic deformation and do not represent the true damping curves.

In view of the wide scatter of points in Figs. 21 and 22 it would appear as though the author must arrive at the same conclusions as earlier investigators[1] of this subject in that damping is not associated with notch sensitivity.

Written Discussion: By S. L. Case, research supervisor, Jones and Laughlin Steel Corporation, Pittsburgh.

Mr. Brophy's paper is an excellent contribution on a very timely subject. Damping capacity first acquired prominence in German literature a little over a decade ago, when the term "Dampfungsfahigkeit" in reference to metals was made popular by O. Foeppl[2], and correlations of this property with fatigue endurance were attempted. American technical literature seemed to ignore damping capacity of metals until 1928[3], and authentic research on this subject is meager in scope, as evidenced by the bibliography furnished in Mr. Brophy's

[1]Gough and Hanson, *Proceedings*, Royal Society (A) 104, 1923.
Gough, Hanson, and Wright, *Philosophical Transactions*, Royal Society (A), 226, 1926.
O. Foeppl, *Metallwirtschaft*, Heft 18, May 1929, p. 419.
H. Kortum, *Techn. Mech. u. Thermodynamik*, 1, 297, 1930.
H. Fromm, "Nachwirkung u. Hysteresis," *Handbuch d. Phys. u. Techn. Mechanik*, Vol. IV-1, p. 436, 1931.

[2]O. Foeppl, "Drehschwingungsfestigkeit und Dampfungsfahigkeit," Werkstoff Bericht No. 36, *Verein Deutscher Eisenhüttenwesen*, 1923.

[3]R. H. Canfield, "Internal Friction in Metals," *Physical Review*, Vol. 32, No. 3, September, 1928.

paper. This apparent lack of interest is rather difficult to explain. Perhaps we were too busy counting inclusions, or classifying grain-size, and thus hunting for squirrels we missed the elephant.

Damping capacity is defined as "the amount of work dissipated into heat by a unit volume of the material during a completely reversed cycle of unit stress." It is a measure of the internal friction of solids, and being a structure-sensitive property it is bound, by a priori reasoning, to affect profoundly the behavior of the material under conditions of dynamic stress in service. A correlation of this property with resistance to alternating stresses or fatigue endurance, notch fatigue, and corrosion fatigue may thus be logically expected. The importance of correctly establishing such a correlation warrants our being hypercritical in analyzing the data supporting any attempts at such a correlation.

Mr. Brophy deserves considerable credit for introducing the subject at this time, however, the writer feels it is his duty to point out that he disagrees with Mr. Brophy's interpretation of the data submitted, and that the conclusions advanced by Mr. Brophy are not warranted by these data.

Summarizing briefly, Mr. Brophy postulates that:

(1) Large grain-size is associated with a high damping capacity, and vice versa.

(2) High damping capacity is associated with a higher resistance to notch fatigue, and vice versa.

(3) High damping capacity is associated with a low resistance to overstress, under alternating stress, and vice versa.

These postulates necessarily imply that a definite correlation exists between grain-size, fatigue, and resistance to overstress. Very few metallurgists could afford to gloss over such an important correlation, if it is definitely established.

A direct comparison between coarse- and fine-grained steels is furnished by the author in a series of tests made on two 0.36 and 0.37 per cent carbon steels. The data are given in Figs. 6A, 6B, 7, 8A, 8B, 9A, 9B, 15, 16, 17, and 18; they deserve careful scrutiny. The two steels were tested in the annealed, normally quenched and tempered, and in an artificially coarsened state. The microstructure of the steels in the annealed state is not shown, but from the McQuaid-Ehn tests it is a certainty that the difference in their grain-size in the annealed state was very marked, yet, their specific damping capacities in this state, as shown on Fig. 7, were practically identical. The fatigue endurance tests, shown on Figs. 15 and 16, indicate that in the annealed state the notch endurance of the fine-grained steel was considerably higher than that of the coarse-grained steel, i.e., an effect diametrically opposite the one the author's conclusions would lead us to expect. It is only in the artificially coarsened state as shown on Figs. 17 and 18, that the behavior of these steels is predictable from the author's conclusions, but in actual service such steels are, of course, never subjected to such a treatment.

It is the writer's opinion that the only safe interpretation one can place on Mr. Brophy's data is that "when the damping capacity of a steel in the annealed state is lowered by some special treatment, its behavior under alternating stresses and its resistance to notch effect is materially changed, and that

coarse- and fine-grained steels may show a difference in the magnitude of change." Such a conclusion is quite remote from the ones drawn by the author.

Just what is the explanation for the lowering of the specific damping capacity by the grain coarsening treatment we do not venture to guess. The difference in the rate of transformation of coarse- and fine-grained steels at subcritical temperatures is so pronounced that the coarsening treatment undoubtedly introduced a multitude of variables which were bound to affect a structure-sensitive property like damping capacity.

Since 1931, the writer had an opportunity to do considerable research on the damping capacity of carbon steels, and particularly on the correlation of this property with sensitivity of steel to overstrain and overstrain aging, as well as with fatigue endurance. A large number of steels of varying analyses and various steel making and deoxidizing practices were investigated. He will be candid enough to admit that four years' work have convinced him the property of damping capacity is far more complex than it seemed to him in 1931.

A striking example of the difference in behavior of rapidly aging and the so-called "non-aging" steels was brought out in the study of damping capacities of overstrained steels subjected to natural and artificial aging.

The tests were made on the Foeppl-Pertz vibration damping tester, similar to the one used by Mr. Brophy. After determining the damping capacity of a steel specimen in the annealed, normalized, or heat treated condition, the specimen is transferred to a torsion machine, twisted 360 degrees and as rapidly as possible transferred back to the damping tester. Damping curves are then obtained at certain time intervals to study the effect of aging. Duplicate specimens are subjected to artificial aging in the blue-brittleness range.

Damping aging tests carried out in such manner are unusually illuminating. Overstrain results in a marked increase in specific damping capacity. This increase often reaches a magnitude of 1000 per cent at a stress in the neighborhood of 5000 pounds per square inch. This increase is not of a permanent nature. The acquired damping capacity is gradually, but constantly lowered in the course of time. Apparently aging and non-aging steels behave similarly in this respect. Overstrain raises their damping capacities to the same extent, but under aging influences this damping capacity is lowered at greatly different rates. On some steels the damping capacity drops to the original level of the normalized state in 24 hours, on others after 6 months' aging the damping capacity is still 100 per cent higher than in the normalized state.

The unexpected feature of this test is that artificial aging for one-half hour in the blue-brittleness range brings down the damping capacity of both aging and non-aging steels to a lower level than that of the annealed or normalized state. The overstrain-damping capacity thus not only serves as an exceptionally sensitive method for the study of aging phenomena, but points to the thought that there is not only a quantitative, but a qualitative difference between natural and artificial aging, since under such a test steels showing enormous difference in their natural aging rate show a similar aging capacity under artificial aging treatment.

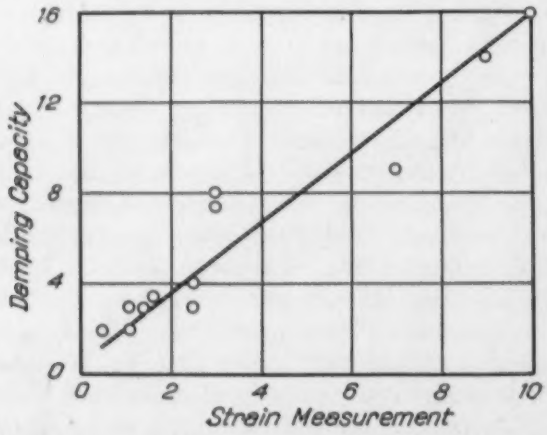
The writer's experiments are mentioned here merely to point out the

multitude of variables which might conceivably influence the damping capacity without a corresponding effect on other physicals. This discussion of Mr. Brophy's paper is not intended in the spirit of destructive criticism. The writer realizes, however, the far reaching importance and implications of the author's conclusions, and wishes to sound a warning of caution in the proper interpretation of the data contained in Mr. Brophy's otherwise truly excellent paper.

Oral Discussion

S. L. Hoyt:[4] After some study of this paper by Mr. Brophy it seemed that possibly there was something lacking in the data, and it occurred to me that if we had measurements of strain in as complete detail as those for stress, a fundamental contribution might be made to the problem of damping capacity. Mr. Brophy gives no strain measurements but the damping capacity is a phenomenon of hysteresis, or is some sort of a combination of stress and strain. By dividing the damping capacity by the stress I would get a figure which must have the dimensions of strain, or at any rate I made that assumption and proceeded as follows.

The fatigue limits reported in the paper were divided by 0.5 (rather than by 0.55) and for those values of the stress I secured the damping capacity. By dividing this figure by the stress I got a figure which I called strain. The dimensions are perfectly arbitrary, it is true, but when I plotted points obtained in this way, the strain at the fatigue limit was found to be nearly a straight line function of the damping capacity. See Fig. accompanying this discussion. Both of the factors correlated in this way varied by about an order of magnitude, which will give an idea of the range covered



by the figures. Twelve points in all were calculated, as is shown by the attached figure.

If the assumption is correct what it means is that the greater the damping capacity, the greater is the strain which the material is able to withstand; or in other words, the greater is the strain at the fatigue limit. I would suggest to Mr. Brophy that he try to include strain measurements in

[4]Director of Research, A. O. Smith Corp., Milwaukee.

his fatigue testing to see if that does not add a factor which will help him explain the things that he observes.

So far I have said nothing about the notch effect but it seems to me that there is apt to be a misunderstanding here. In other words the fatigue test on a notched bar does not correlate with the single blow impact test on a notched bar. Mr. Brophy makes no such assumption, but I think the point ought to be emphasized. Professor Ludwig has recently shown that an aged condition in steel which gives a very low notched bar value does not materially lower the notched fatigue limit. In other words the fields covered by the two tests are quite different, though possibly if both were studied sufficiently there would be some overlapping.

Mr. Brophy, by means of his paper, covers a field which is extremely important and also very broad. It is a valuable contribution and I trust we may have more from his pen.

A. V. DE FOREST:[8] The damping capacity of a metal seems to be looked upon as something that has a definite value if measured under definite conditions, whereas after using the torsion test and various other methods of obtaining a similar measure of elastic behavior, such as damping out of longitudinal sound waves, it appears that there is a whole range of damping capacities, depending not only on the frequency of the applied stress and the range of stress but depending also on very small degrees of overstrain that have been applied to the material. I wonder if we do not have to define what we are talking about a little better.

I have found, for instance, that it requires an exceedingly small amount of overstrain in a test specimen to change the damping capacity enormously, by 50 per cent or more, and that a very moderate degree of aging on top of that overstrain will restore the damping capacity to a minimum, which may be far below the original measurement. In that case we are faced with the added complication that small overstrains on a notch may result in changing the damping capacity of a notch bar over a range which is far greater than that between one type of steel and another.

We need better methods of measurement and a better understanding of the variables involved in a damping test before trying to correlate really accurately with such complicated phenomena as the notch fatigue value of material.

In the study of springs, there has been a good deal of work done on hysteresis under slowly repeated loads, and in that case we have found that the method of preparation of a spring which gave the minimum hysteresis under slowly repeating loads was also the method which gave the minimum hysteresis under the Foeppl test, and also the minimum in high frequency tests all the way up to 100,000 cycles. This would indicate that the damping test is really measuring a condition which is fundamentally important.

J. F. CUNNINGHAM:[9] After hearing Mr. Brophy's paper this afternoon, I feel that this, my first convention, has been worthwhile. The present speaker is just starting a very small part in the investigation of a large turbine shaft which has developed a fatigue fracture. As you know these are vertical

[8]Associate Professor of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

[9]Superintendent of Testing Laboratories, Civil Engineering Dept., University of Manitoba, Winnipeg, Canada.

shafts without any bottom bearing and it would seem, looking at it from information gained from this paper, we may be able to find answers to some of the various questions. It may be possible to get some actual stress or strain readings in this case and so the information gained from this one paper has made it worthwhile coming from the Canadian West to hear what has been accomplished by the research men of the United States.

Author's Closure

I wish to thank the gentlemen who have contributed to the value of my paper through their discussions, whether favorable or adverse. The latter, especially, are of great value in that they stimulate additional research and sound the words of caution against too readily accepting these progress reports as finished jobs.

Some of the questions brought out in these discussions can only be answered after further work. Dr. Hoyt's strain factor is one of these. His speculations are interesting and especially stimulative of additional study, but at the present time the author is at a loss for the interpretation.

It may be of interest that the closing of the damage area at high stresses which Professor Moore mentions has been determined on two materials. One, an almost pure iron, was determined quite completely and the area formed resembles an hysteresis loop.

Regarding the speed of testing, also discussed by Professor Moore, we have recently made some tests at 20,000 cycles per minute on three steels which seems to indicate that the influence of speed of testing depends upon damping capacity. We have found, for instance, higher endurance limits for low damping steels and lower limits for high damping.

The notch sensitivity and the damage by overstress is increased and apparently, although our data are insufficient to draw definite conclusions, low damping steels are affected by speed to the greater extent. Many more data are required for definite conclusions and it is hoped that this will be a subject for a future publication.

In reply to Mr. Harper's questions; first, the two C steels of different inherent grain-sizes were obtained from one of the large steel companies, and it is assumed that the fine grain-size was obtained by aluminum additions, and as stated, undoubtedly some of the effect is the result of the presence of finely dispersed alumina.

The nickel-chromium steel used in our experiments was treated in the form of 1⅛-inch round bars and was drawn for two hours at temperature. While the steel cooled in the furnace from the drawing temperature certainly was exposed to tempering action for a longer time, the tensile properties were but slightly different and probably account for the difference found in the endurance limits.

It was not assumed, as Mr. Harper states, that the same heat treatment for the coarse- and fine-grained carbon steels would result in similar structure and physical properties. It was realized that the properties would differ and it was desired to determine the difference in damping capacity resulting from the difference in the nature of the steels. His supporting statement is true only for low stresses. In the range of stress above 20,000 pounds per square inch the fine-grained steel, coarsened, shows a smaller increase over the fine-

grained steel than does the coarse-grained steel, coarsened, over the coarse-grained steel.

As a matter of fact, a comparison of the grain-sizes as indicated in the micrographs, in Figs. 8A and 9A, are not very different.

The damage line, or that portion of it which we have located, for the inherently coarse-grained steel is about as low as it can be. Obviously, it cannot be located below the endurance limit. Therefore, if enlarging grain-size tends to increase the damage by overstress only a fine-grained steel with a high damage line could be affected. It is believed, however, that differences will be found in the size of the damage areas, when these are completely determined.

Professor Jasper's comments are appreciated. He suggests that notch sensitivity is associated with discontinuities, in spite of the fact that cast iron which is full of discontinuities is among the least sensitive to external notches.

Mr. Horger questions the stability of the damping characteristics of the steels tested. As was stated in the paper, it is recognized that the damping capacity changes with time under repeated constant stress and approaches a constant value, or not, depending upon the value of the stress. It is believed, however, that the change with time is dependent upon the initial damping.

I cannot agree with Mr. Horger that the damping curves as presented involve both elastic and plastic deformation. In any stress cycle during the free vibration, both plastic and elastic deformations are present, it is true, but the decrease in amplitude between two successive cycles represents plastic deformation only.

In spite of the wide scatter of points in Fig. 22, which is due in all probability to the use of the average value (0.55) for the ratio between shear stress and tension stress, the conclusion was arrived at that notch sensitivity does increase rapidly with decreasing damping, particularly below a limiting value which may vary somewhat with the severity of the notch.

If the most representative curve is drawn among the points of Fig. 22, excluding those for cast iron and the two annealed 0.36 carbon steels, but including that point mentioned in the text for the austenitic steel, and calculations made for the ratio of shear to tension stresses, it will be found that most of the values so determined will fall within the limits of 0.44 to 0.71. This indicates that most of the scatter is the result of using the average value of 0.55 instead of the actual value for each test.

I am pleased to receive the comments of both Mr. De Forest and Mr. Case in view of their extensive work in this field. The dependence of damping capacity upon previous history which both speak of is realized, and an effort was made to keep constant as many of the variables as possible.

There is an error in Mr. Case's discussion which, however, may be typographical. The damping capacity of a steel is increased by grain coarsening treatment, not lowered as stated by Mr. Case.

The postulates listed by Mr. Case are among the only conclusions one may draw from the data submitted.

Mr. Cunningham's remarks are indeed very flattering, and trust he will not be disappointed as to the value of this work.

FACTORS INFLUENCING THE NATURE OF THE CUTTING SPEED–TOOL LIFE CURVE

By O. W. Boston, W. W. Gilbert, and C. E. Kraus

Abstract

For rating the machinability of a metal, with tool life as a basis, it is advisable to determine the cutting speed-tool life curve for desirable conditions, rather than to base conclusions on the tool life for one cutting speed determined for each of the variables. Results of tests are presented in this paper to show that this straight-line curve, as plotted on log-log paper, may be changed in its vertical position on the scale and in slope from the horizontal, if any one of the factors, such as type of tool material, tool shape, the shape of the cut, the analysis or structure of the material cut, and the cutting fluid, are changed.

Four brands of high speed steels are shown to produce four distinctly different cutting speed-tool life curves when cutting a given steel under otherwise the same conditions. Curves of different height and slope are obtained when cutting steels of different analyses with the same tool material and tool shape, and when the heat treatment of steel of a particular analysis is changed. If the tool angles, comprising the back-rake, side-rake, side-cutting angle, and the tool nose radius, are changed, different cutting speed-tool life curves are obtained.

It is shown further that, when cutting one steel with each of several cutting fluids with a constant tool shape and a deep thin cut, one set of cutting speed-tool life curves is obtained. When the cut is shallow and thick but of the same cross sectional area, distinctly different curves are obtained for each of the same group of cutting fluids. Lastly, it is shown that, when cutting a given steel with a given tool and size of cut, individual cutting speed-tool life curves are obtained for each of several cutting fluids. Those cutting fluids having supposedly superior lubricating properties appear to have less slope from the horizontal and are, therefore, superior for metal cutting where a long tool life accompanied by a low cutting speed is desired.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, from September 30 to October 4, 1935. Of the authors, O. W. Boston is professor and W. W. Gilbert and C. E. Kraus are instructors in the Department of Metal Processing, University of Michigan, Ann Arbor, Michigan. Manuscript received May 6, 1935.

THE object of this paper is to present the results of various tests in turning to show that the exponent, as well as the constant, in the formula $VT^n = C$ may vary as conditions are changed. It is shown that the relation between the cutting speed and tool life conforms to the above mathematical equation, in which V is the cutting speed in f. p. m.; T is the tool life under cut up to the time of tool breakdown, measured in minutes; n is the exponent of T

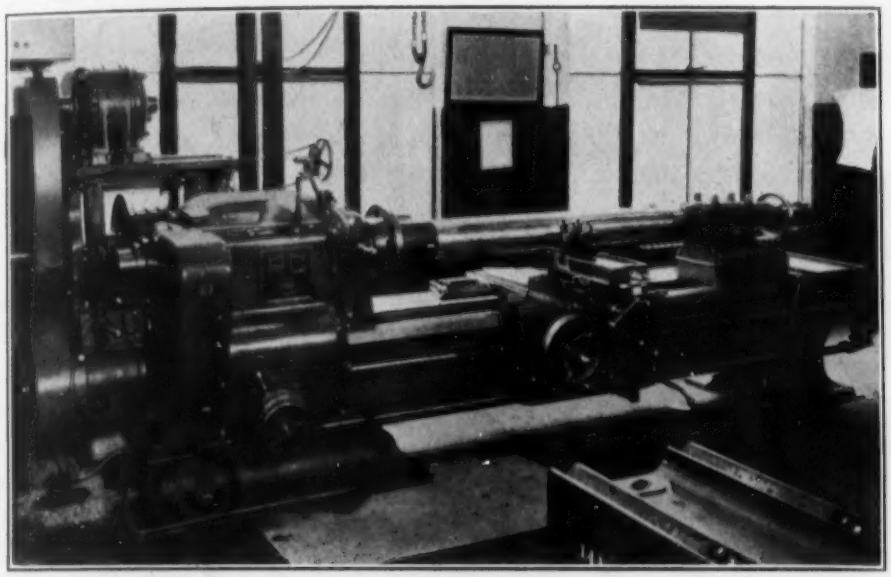


Fig. 1—The 30-Inch Swing Variable Speed Lathe Used in the Tests.

and equals the tangent of the angle of slope of the cutting speed-tool life curve when plotted on log-log paper; and C is a constant depending upon the various conditions.

In order to show the influence of each of several factors, such as the tool material, the tool shape, the material cut, and the cutting fluid, the results of several sets of tests are presented and discussed. It is shown that a variation in any of these factors may change the value of n as well as the constant C in the above equation.

Equipment and Methods Used in the Cutting Speed-Tool Life Tests

In running the various cutting speed-tool life tests, two set-ups were used: one consisting of a heavy-duty lathe having a 30-inch swing and 14-foot bed with a 12-speed geared head, as shown in

Fig. 1; and a second a 14-inch swing, 6-foot bed, having a 16-speed geared head drive. The large lathe was driven by a constant speed motor operating through a variable speed transmission which, in turn, drove the driving pulley of the geared head so as to provide any slight change in cutting speed desired. The smaller lathe was operated by a direct current motor provided with a 66-point rheostat to furnish 66 speed steps for each of the 16 speeds of the geared head.

In both lathes the tool bits were clamped into a special tool holder by set screws. The holder, in turn, was clamped to the carriage by straps in the usual manner.

The tool life in minutes was measured by means of a stop watch and was the time from the start of the cut until tool failure, as indicated by the sudden breaking down of the cutting edge. The cutting speed was measured by means of a cut meter operating on the surface of the test log just ahead of the tool.

Both lathes were equipped with a cutting-fluid circulating system, and the cutting fluid was directed vertically downward on the face of the tool. In the Ryerson lathe a full stream from a ¾-inch pipe flowed on the tool at the rate of 4.5 gallons per minute. In the Monarch lathe a full stream from a ½-inch diameter pipe flowed on the face of the tool at the rate of 4.75 gallons per minute.

The Tools Used

Cutting tools in the form of standard ⅜-inch square tool bits consisting of five different brands of high speed steel, as shown in Table I, were used. Tool bits have been used in these tests, inasmuch as they are small, inexpensive, and convenient to grind. Previous tests have indicated that the size of the tool has practically no influence on its performance, other conditions remaining constant. These bits can be reground a number of times and still produce the same cutting performance. Forged tools are apt to vary in their performance after each forging and subsequent heat treatment, and usually require a greater amount of preparation for use.

The tool bit holder used in all turning tests is illustrated, with its nomenclature, in Fig. 2. The bits were ground while being held in this or a similar tool holder. The names of the various angles and parts are given. A special machine has been developed for grinding the single point tools with a cup-shaped wheel. The tool and holder were clamped in a universal vise which can be set suc-

cessively to each angle. All tools were carefully ground and reground dry. Burrs were removed by a light hand honing after grinding. The tools for a given test were grouped in sets of six or eight and were reground and used again numerous times so as to reduce to a minimum the variation of tool material.

In grinding the nose radius, the tools first were ground to a

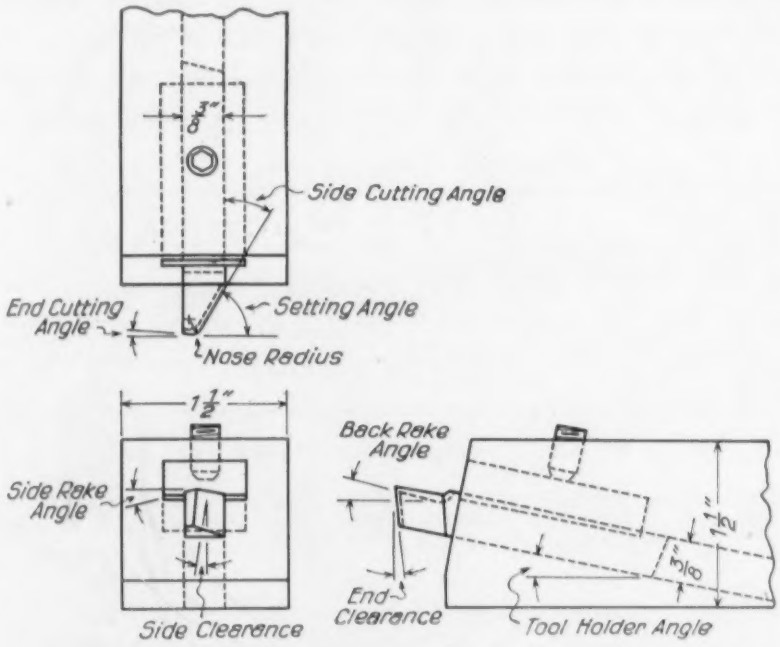


Fig. 2—The Tool Bit Holder Used in the Turning Tests, With Nomenclature.

sharp point, after which the radius was ground by hand to conform with a radius gage. They were honed before the final checking. This method was found to give consistent results.

A convenient designation for each tool shape has been developed and used successfully by the authors for a period of years. A specific tool shape may be designated as 8-14-6-6-6-15-3/64-R. These values in the order named are 8-degree back rake, 14-degree side-rake, 6-degree front clearance, 6-degree side clearance, 6-degree end-cutting angle, 15-degree side-cutting angle, and 3/64-inch nose radius. This "Standard" tool shape was used in many of the following tests. The tool holder and bit were clamped at right angles to the axis of the work so that the side-cutting edge of a tool having

a 15-degree side-cutting angle produced a setting angle with the axis of the work of 75 degrees.

Influence of Tool Shape on the Cutting Speed-Tool Life Curves

In a recent paper[1] it was shown that, when turning an S.A.E. 2335 forged steel test log, the values of the constant (1) increased as the nose radius was increased from zero to ¼ inch, (2) increased as the side-cutting angle was increased from zero to 60 degrees, (3) increased as the side-rake angle was increased from zero to 22 degrees. (it dropped off again for 30 degrees, and (4) remained practically

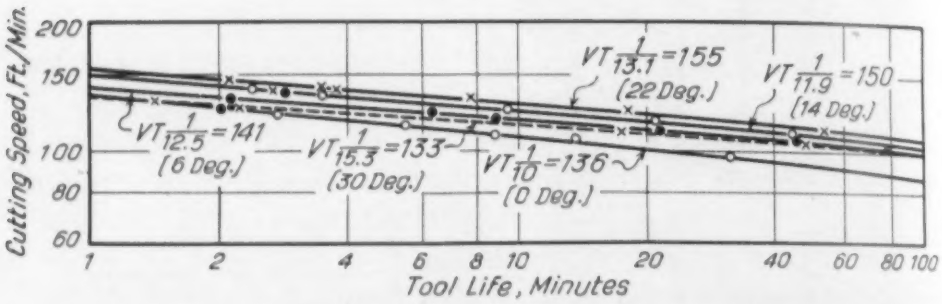


Fig. 3—Cutting Speed-Tool Life Curves for Each of Several Side-Rake Angles on the "Standard" Tool of Type *C* High Speed Steel, When Turning S.A.E. 2335 Steel with a Feed of 0.0125 Inch and a Depth of Cut of 0.100 Inch.

constant as the back-rake angle was increased from zero to 16 degrees. The values of n in the equation also were shown to vary as the nose radius, side-rake angle, and back-rake angle were increased.

Bits, type "C" of Table I, ⅜ inch square of regular 18-4-1 high speed steel were used when taking a depth of cut of 0.100 inch and a feed per revolution of the work of 0.0125 inch. To illustrate this effect, the various cutting speed-tool life curves are shown in Fig. 3 for a given tool ground successively to side-rake angles of 0, 6, 14, 22, and 30 degrees. The corresponding values of n are 1/10, 1/12.5, 1/11.9, 1/13.1, and 1/15.3, respectively, as represented graphically in the upper part of Fig. 4. Fig. 4 also shows the values of the cutting speed for each of the side-rake angles for a tool life of 10, 20, 60, 90, and 300 minutes. For the 20-minute tool life, the allowable cutting speeds for various side-rake angles of 0, 6, 14, 22, and 30 degrees are 101, 111.5, 118, 122, and 110, respectively.

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[1]O. W. Boston and W. W. Gilbert, "The Life of Turning Tools as Influenced by Shape," TRANSACTIONS, American Society for Metals, Vol. 22, No. 6, June 1934, p. 547.

Table 1
Cutting Tools Used in Cutting Fluids Tests

All bits of a kind were from the same ingot, treated at the same time, and tested for uniformity. All were ⅜-inch square section.

Bit Letter	Material	Heat Treatment	Analysis Mo	Analysis Co	Analysis C	Analysis W	Analysis Cr	Analysis V	Rockwell "C" Hardness
A	18-4-1 High speed steel	Quench at 2300 degrees Fahr. Draw at 1060 degrees Fahr.			0.70	18.62	4.59	0.93	
B	18-4-1 High speed steel	Quench at 2360 degrees Fahr. Draw at 1060 degrees Fahr.			0.77	17.64	4.09	1.38	64.6–65.0
C	18-4-1 High speed steel	Quench at 2400 degrees Fahr. Draw at 1100 degrees Fahr.			0.76	18.22	4.06	1.08	64.0–67.0
D	Cobalt high speed steel	Quench at 2400 degrees Fahr. Draw at 1080 degrees Fahr.	0.50	4.75	0.70	18.00	4.00	1.00	64.0–65.0
E	Molybdenum high speed steel	Quench at 2200 degrees Fahr. Draw at 1025 degrees Fahr.	8.00		0.78	1.50	3.75	1.00	65.0–66.0

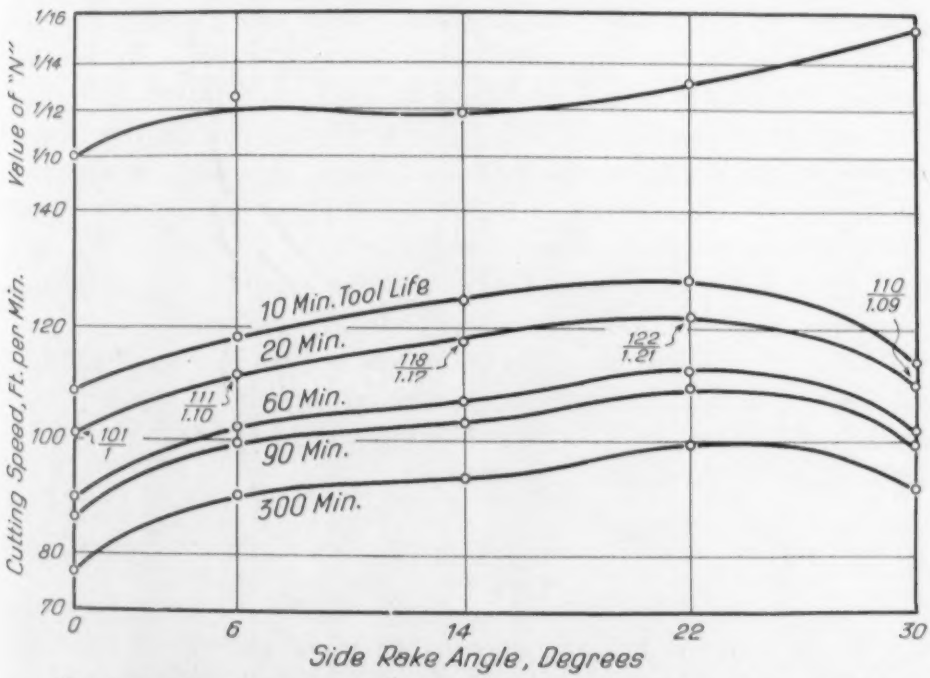

Fig. 4—Cutting Speeds for Various Side-Rake Angles for Each of Several Values of Tool Life as Determined from Fig. 3.

Influence of Various Types of High Speed Steels on the Cutting Speed-Tool Life Curves

A series of cutting speed-tool life tests was run with each of

four high speed steel tool bits referred to as A, C, D, and E in Table I, ground to the "Standard" shape, when turning the S.A.E. 2345 steel dry in the 14-inch lathe. All other conditions were kept constant, as listed in Table II. The experimental data, when plotted on log-paper in Fig. 5, gave four straight lines. The formulas representing these curves

Table II

A Summary of Tool Life-Cutting Speed Relation for Various Tool Materials when Turning S.A.E. 2345, dry. The feed was 0.0255 inch per revolution and the depth of cut was 0.050 inch. The tools were ⅜-inch square section and of the "Standard" shape 8-14-6-6-6-15-3/64-R.

Tool Material	Cutting Speed-Tool Life Equations	Cutting Speed for 20 Minutes	Cutting Speed for 2 Hours
A	$VT^{1/9.8}=126$	92	78
C	$VT^{1/11}=146$	111	95
D	$VT^{1/8.1}=142$	97.5	78.5
E	$VT^{1/10.1}=136$	102	86

are shown in Table II, together with the cutting speeds in f.p.m. for each a 20-minute and a 2-hour tool life. In this discussion the constants are of minor importance. The curves show that each tool material produces a characteristic slope, as represented by the values of the exponent of T in Table II. The authors have found in tests on other steels with these same tools that other values of slope may be obtained and that the vertical position of the lines may be changed, that is, one tool showing superior results on one steel may show medium or inferior results on another steel. It is interesting to note that the top and bottom curves in Fig. 5 are produced by A and C, both generally used regular 18-4-1 types of high speed steel. The two intermediate curves are for cobalt high speed steel and molybdenum high speed steel.

Influence of the Material Cut on the Cutting Speed-Tool Life Curves

In the tests involving various materials cut and cutting tools, the two steels listed in Table III were used extensively. The 6-inch diameter S.A.E. 2345 steel was used in the 14-inch lathe, and the large forging of S.A.E. 3140 steel was used in the 30-inch lathe.

Many examples indicate that the analysis or condition of the steel cut influences the exponent n and the constant C in the cutting speed-tool life equation. The equations for several different analyses

and
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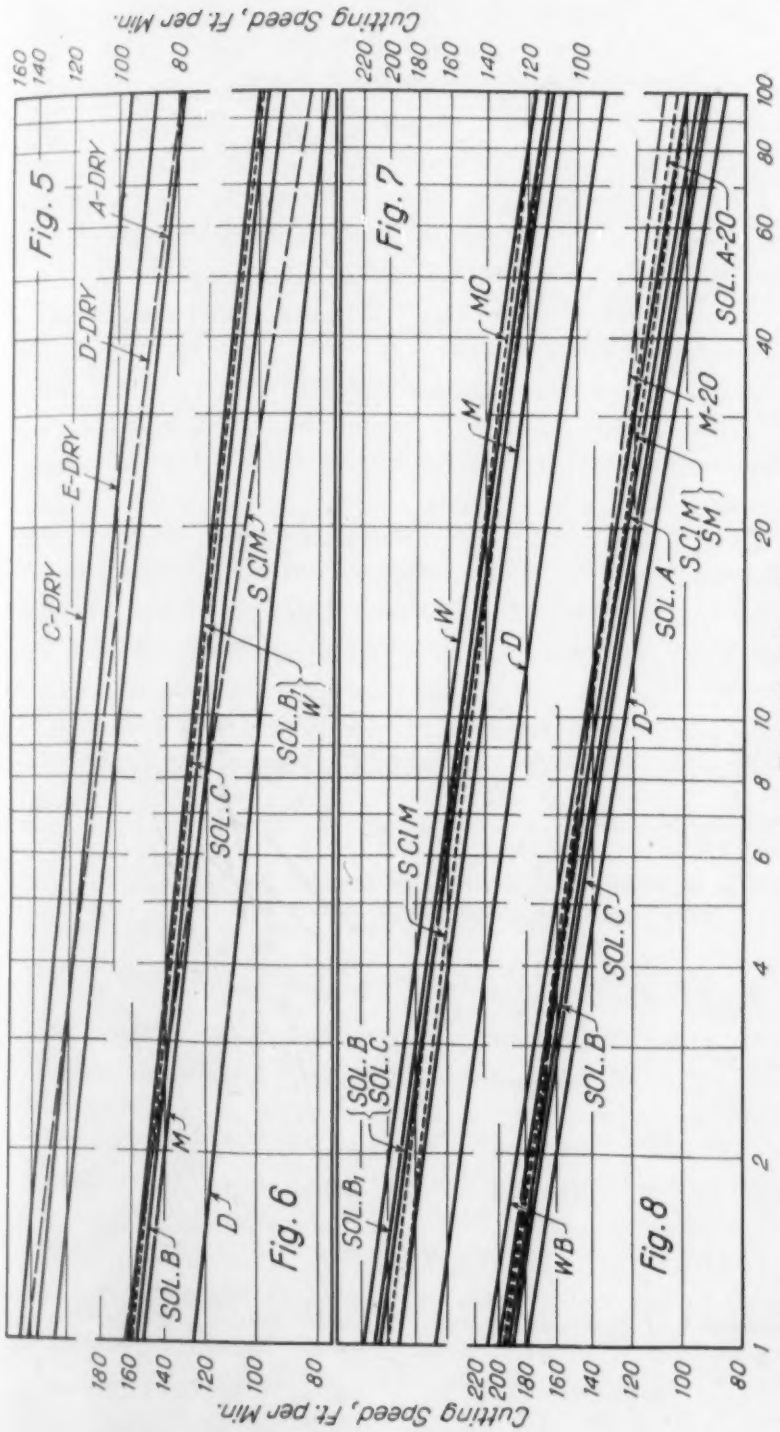


Fig. 5—Cutting Speed-Tool Life Curves for Various Types of High Speed Steels Plotted on Log-Log Paper, when Turning an S.A.E. 2345 Steel. Cutting was Dry with the "Standard" Tool Shape. The Feed was 0.0255 In. The Depth of Cut 0.050 In.

Fig. 6—The Influence of Various Cutting Fluids on Cutting Speed-Tool Life Curves Plotted on Log-Log Paper. Tool Material A, 18-4-1 High Speed Steel, of Table I was Used When Ground to the Standard Tool Shape of 8-14-6-6-15-4-R, When Cutting S.A.E. 2345 Steel Annealed, with a Feed of 0.0255 Inch and a Depth of Cut of 0.050 Inch (Data by C. N. Rix and W. G. Starr).

Fig. 7—Cutting Speed-Tool Life Curves Similar to Those in the Above Figure, with a Feed of 0.0127 In. and a Depth of Cut of 0.100 In.

Fig. 8—Cutting Speed-Tool Life Curves on Log-Log Paper for Various Aqueous Cutting Fluids.

and conditions of materials when cut dry under specific conditions are summarized in Table IV. Two different equations are obtained when

Table III
Materials Used in Cutting Fluids Tests

Material	Size	Analysis C	Mn	S	P	Si	Ni	Cr	Brinell Hardness
S.A.E. 2345 Annealed	6-inch diameter rolled and machine straightened	0.49	0.70	0.025	0.015	0.210	3.41	0.04	Av. 197
S.A.E. 3140 Normalized and annealed, 1500 degrees Fahr. for 7 hours air cool 1200 degrees Fahr. for 8 hours furnace cool	Forging 14 inches in diameter and 48 inches long	0.42	0.69	0.021	0.017	0.17	1.41	0.61	Av. 190

cutting the S.A.E. 2345 steel annealed as the size of the cut is changed, the area, however, remaining constant. The equation for the S.A.E. 3140 normalized and annealed steel cut with a different brand of high speed steel is still different from those curves for the S.A.E. 2345 steel.

In turning cast steel containing 25 per cent chromium and 10 per cent nickel with tool E of Table I, ground to the "Standard"

Table IV
Influence of Analysis and Condition of Steel on the Cutting* Speed-Tool Life Equation When Cutting Dry

Material	Tool Type	Tool Shape	Feed	Depth of Cut	Equation
S.A.E. 2345, annealed (See *D*, Table VI)	*A**	"Standard" 8-14-6-6-6-15-3/64R	0.0255	0.050	$VT^{1/9.6}=126$
S.A.E. 2345, annealed (See *D*, Table VI)	*A**	"Standard"	0.0127	0.100	$VT^{1/7.3}=168$
S.A.E. 3140, normalized and annealed. (See *D*, Table VII)	*B**	"Standard"	0.0125	0.100	$VT^{1/6.3}=178$
25% Cr., 10% Ni Steel, as cast	*E**	"Standard"	0.025	0.050	$VT^{1/14.3}=46$
25% Cr., 10% Ni Steel, quenched at 2000 deg. F.	*E**	"Standard"	0.025	0.050	$VT^{1/6.4}=46$
S.A.E. 3140A heat treated	18-4-1	6-12-6-6-13-0-1/8R	0.037	0.0625	$VT^{1/4.75}=100$
SA.E. 3140A annealed	18-4-1	6-12-6-6-13-0-1/8R	0.037	0.0625	$VT^{1/7.06}=125$
S.A.E. 1340A annealed	18-4-1	6-12-6-6-13-0-1/8R	0.037	0.0625	$VT^{1/3.33}=244$
S.A.E. 1340A spheroidized	18-4-1	6-12-6-6-13-0-1/8R	0.037	0.0625	$VT^{1/4.12}=188$
S.A.E. 1340A (modified) heat treated	18-4-1	6-12-6-6-13-0-1/8R	0.037	0.0625	$VT^{1/3.8}=130$
S.A.E. 1340A spheroidized	18-4-1	6-12-6-6-13-0-1/8R	0.037	0.0625	$VT^{1/4.36}=168$

*Table I.

shape, when taking a cut 0.050 inch deep and 0.0255 inch feed per revolution, it was found that, when machining the bar as cast, the value of n was 1/14.3, but when machining a corresponding bar after quenching at 2000 degrees Fahr., n was increased to 1/6.4, as shown in Table IV. This shows a considerable change in the value of the exponent merely through a change in structure. For a tool life of 1 minute, the cutting speed for each curve is 46 f.p.m., but for a 60-minute tool life, the cutting speed for the heat treated bar is 25 f.p.m., and that for the as-cast bar is 35 f.p.m.

When an S.A.E. 3140A steel is machined under identical conditions, except being heat treated in one instance and annealed in the second, two widely different equations are obtained, as shown in Table IV. Similarly, when S.A.E. 1340A steel is machined, under the same conditions, except that it is annealed in one case and spheroidized in the second, the equations differ considerably. The same holds true when machining the S.A.E. 1340A (modified) steel in the heat treated and spheroidized condition, all shown in Table IV. From these data, which have been obtained under very carefully controlled conditions, it is observed that the analysis and structure of the metal, as determined by its heat treatment, very greatly affects the exponent and constant of the cutting speed-tool life equation.

Influence of Cutting Fluids on Cutting Speed-Tool Life Curves

Influence of Shape of Cut on Effect of Cutting Fluids

A series of tests, using the S.A.E. 2345 steel shown in Table III on the 14-inch lathe with tool A of Table I for each of several cutting fluids, was run and curves, as shown in Figs. 6 and 7, determined. In Fig. 6 the depth of cut was 0.050 inch and the feed 0.0255 inch. Each curve is labeled by a symbol to indicate the cutting fluid referred to in Table V. Similar data are shown in Fig. 7, in which the size of the cut was changed to a depth of 0.100 inch and a feed of 0.0127 inch. The area of cut, however, remained constant.

Comparing the corresponding curves of Figs. 6 and 7, it is seen that those of Fig. 7 all are higher than those of Fig. 6, indicating that the shape of the cut for constant area has an influence. The influence of the exponents and constants for both sets of curves

Table V
Cutting Fluids Used in Cutting Fluids Tests

Symbol	Cutting Fluid
D	Dry cutting
W	Water, distilled
WB	Water, distilled, plus 1½ per cent of borax by weight
Emulsion A	Soluble oil "A", 1 part to 16 parts of water
Emulsion B	Soluble oil "B", 1 part to 16 parts of water
Emulsion B1	Soluble oil "B", 1 part to 8 parts of water
Emulsion C	Soluble oil "C", 1 part to 16 parts of water
M	Mineral oil, light, 110 Saybolt seconds at 100 degrees Fahr.
MO	Mineral oil, plus 5 per cent Oleic acid
SM	Sulphurized mineral oil (4 per cent sulphur), 110 Saybolt seconds at 100 degrees Fahr.
S Cl M	Sulpho-Chlorinated mineral oil

is summarized in Table VI. In Fig. 6 the slopes of most curves are less than the slopes of those in Fig. 7, giving values of 1/9.6 for several of the curves in Fig. 6 and 1/7.3 for several of those in Fig. 7. A detailed study of the curves of Fig. 6 shows that the value of n, as summarized in Table V, is 1/9.6 for dry cutting and all of the aqueous solutions. It increases to 1/9.1 for the straight mineral oil, and increases further to 1/7 for the sulpho-chlorinated mineral oil. Similarly, in Fig. 7 all aqueous solutions have a value of 1/7.3. This exponent is reduced to 1/7.8 for mineral oil, and reduced further to 1/8.4 for the mineral oil oleic acid and the sulpho-chlorinated oil. The oils for the thick shallow chip of Fig. 6 give the greatest slope of the curve, whereas for the thin deep chip of Fig. 7, the values of n are low. This indicates a more nearly horizontal line, which is very beneficial for long values of tool life at comparatively low speeds.

The above tests show that the thick shallow cut materially reduces the slope of and lowers the cutting speed-tool life curves for all aqueous solutions, producing unfavorable results for fast cutting. Oils are beneficial for the thin deep cut but detrimental for the thick shallow cut.

Influence of Aqueous Solutions

A number of tests were run on the S.A.E. 3140 steel listed in Table III. The 30-inch lathe of Fig. 1 was used. Tool bits ⅜-inch square of 18-4-1 high speed steel were used of a brand different from that used in the previous experiments. The tools were ground to the same "Standard" shape, however. The size of all cuts was 0.0125 inch feed per revolution and 0.100 inch deep.

Preliminary tests were run with several commercial types of

Table VI

A Summary of Tool Life-Cutting Speed Relation for Various Cutting Fluids when turning an S.A.E. 2345 steel, using tools of material "A", 18-4-1 high speed steel, having the shape 8-14-6-6-6-15-3/64-R

Cutting Fluid	Feed in In./Rev.	Depth of Cut in In.	Cutting Speed-Tool Life Equation	Cutting Speed for 20 minutes	Cutting Speed for 2 hours
D	0.0255	0.050	$VT^{1/9.6}=126$	92	78
W	.....	....	$VT^{1/9.6}=161$	118	99
Emulsion B	.....	....	$VT^{1/9.6}=157$	115	96
Emulsion B1	.....	....	$VT^{1/9.6}=161$	118	99
Emulsion C	.....	....	$VT^{1/9.6}=160$	117	98
M	.....	....	$VT^{1/9.1}=152$	109.5	91
S Cl M	.....	....	$VT^{1/7}=163$	105	82
D	0.0127	0.100	$VT^{1/7.3}=168$	113	91
W	.....	....	$VT^{1/7.3}=219$	145	115
Emulsion B	.....	....	$VT^{1/7.3}=208$	138	110
Emulsion B1	.....	....	$VT^{1/7.3}=211$	140	112
Emulsion C	.....	....	$VT^{1/7.3}=207$	137	109
M	.....	....	$VT^{1/7.3}=192$	130	105
MO	.....	....	$VT^{1/8.4}=200$	141	116
S Cl M	.....	....	$VT^{1/8.4}=193$	136	113

aqueous cutting fluids. The results are plotted in Fig. 8. The symbols refer to the cutting fluids in Table V. All five lines are parallel, giving the same exponent in the equation, as indicated in Table VII, but giving constants varying in order from the highest curve down of 207, 198, 192, 189, and 176, respectively, showing borax water to be the best, dry cutting the poorest, and the three emulsions intermediate. It is of interest to note that the exponent of these five equations is 1/6.3 as compared with 1/7.3 for the corresponding cutting fluids for the same size of cut in Table VI. The tool material and steel cut were different in the two tests.

Emulsion A, Emulsion B, and Emulsion C of Fig. 8, consisting of three different commercial soluble oils, were reduced with 16 parts of distilled water.

Influence of Colloidal Graphite in an Emulsion

The next series of tests involved the addition of various proportions of colloidal graphite in Emulsion A. Colloidal graphite, being a nonreversible colloid, is not available in a dry state but is obtainable commercially in concentrated suspension in fluid carriers. When used with emulsions, as in these tests, it was suspended in water and obtained in the form of "Aquadag," a trademarked product furnished by the Acheson Colloids Corporation. "Aquadag" is a concentrated colloidal suspension of graphite in distilled water. The graphite content of this product is 22 per cent by weight, equiva-

lent to 0.015 pound per liquid ounce. Five types of Emulsion A were used containing colloidal graphite in pounds per gallon of emulsion as follows: 0, 0.0075, 0.015, 0.0225, and 0.03 (equivalent to ⅜ of 1 per cent by weight), respectively. These are represented by the cutting fluids in Table VII, indicated respectively as Emulsion A, Emulsion A-1/2-A, Emulsion A-1-1/2-A, and Emulsion A-2-A. The resulting equations are shown in Table VII.

The exponents of the equations for Emulsion A and Emulsion A-1/2-A equal 1/6.3. The exponent is reduced to values of 1/6.5, 1/6.75, and 1/7.1, respectively, for the emulsions containing the greater quantities of graphite, indicating that the curves become slightly more horizontal as the graphite content is increased.

The curves on log-log paper appear as straight lines which are not parallel but cross at a point equivalent to a tool life of 7 or 8 minutes. The values of the constants of the equations are gradually reduced as the slope of the curve is reduced, showing that for the higher speeds, giving values of tool life below 7 or 8 minutes, those cutting fluids having the least amount of graphite are superior. However, for values of tool life above 7 or 8 minutes, those cutting fluids having the greatest amount of graphite become superior.

The commercial use of colloidal graphite suspended in water as an addition to an emulsion is not recommended, because of certain objectionable features encountered. The finish produced seemed to be slightly inferior as the amount of graphite was increased. The cutting fluid was black and extremely dirty. Wherever it splashed and dried, black spots were left which were removed with difficulty.

Influence of Colloidal Graphite in a Soluble Oil

In view of the difficulties encountered with the use of colloidal graphite suspended in water, a series of experiments was undertaken with colloidal graphite suspended in oil. This mixture was added to the soluble oil before being reduced with 16 parts of distilled water. The commercial soluble oils used apparently carried in suspension a saturated content of mineral oils, so that when the oil containing the colloidal graphite was added to the soluble oil, a slight amount of mineral oil was separated. This did not prove to be a serious matter, however. For commercial use, presumably, this could be overcome by putting the colloidal graphite into the soluble oil at the time of its manufacture. The resultant emulsion appeared

to be a grayish color, rather than black as when graphite in water was used. The particles of graphite appeared to be carried in the oil rather than in the water so that, when the machine and work were splashed with the emulsion made from the soluble oil carrying graphite, it did not dry on as when graphite in water was added to the emulsion.

Colloidal graphite in oil was obtained as "Oildag," a trade-marked product furnished by the Acheson Colloids Corporation. This concentrated suspension contained 10 per cent by weight of graphite. This graphite was added to the soluble oil in quantities in pounds per gallon of emulsion as follows: 0, 0.00625, 0.0125 (0.150 per cent by weight), and 0.025, respectively. The curves on log-log paper show the influence of graphite added to the soluble oil before being made into the emulsions on the cutting speed-tool life curves. The straight emulsion produces the lowest and steepest curve. As graphite is added, the curve becomes more horizontal, pivoting about a point corresponding to a tool life between 1 and 2 minutes. The equations are summarized in Table VII under cutting fluids designated as Emulsion A, Emulsion A-1-0, Emulsion A-2-0, and Emulsion A-4-0.

In order to better show the influence of graphite when added to the soluble oil, the exponents and constants of the equations are plotted as solid lines in Fig. 9 on Cartesian co-ordinates over the amount of graphite per gallon of cutting fluid used. At the left are shown the constants and exponents when graphite suspended in water was used in the emulsion. The lower portion of the figure shows that the constant gradually falls off from 198 to 191 as the amount of graphite is increased from zero to 0.03 pound per gallon. The value of the exponent, however, is shown to be reduced from 1/6.3 to 1/7.1. A further addition of graphite reduces the constant but little, but might reduce the exponent appreciably.

The cutting speeds for three values of tool life of 1 hour, 4 hours, and 16 hours, respectively, are shown at the right in Fig. 9 for the emulsion with various proportions of graphite. The use of graphite in the emulsion produces a favorable increase in cutting speed. Because of the disadvantages, however, as pointed out above, the increased speeds are probably not sufficient to justify the commercial use of colloidal graphite in this manner. The change in tool life for cutting speeds of 70, 85, and 100 f.p.m. is shown in the upper right of Fig. 9 for different amounts of colloidal graphite.

The values of the constants and exponents of the cutting speed-tool life curves obtained with emulsions containing various proportions of graphite suspended in oil are shown as solid lines at the left in Fig. 9. The constant is reduced slightly as the amount of graphite is increased. The exponents, however, are reduced considerably causing the curves to become more horizontal for an increase of

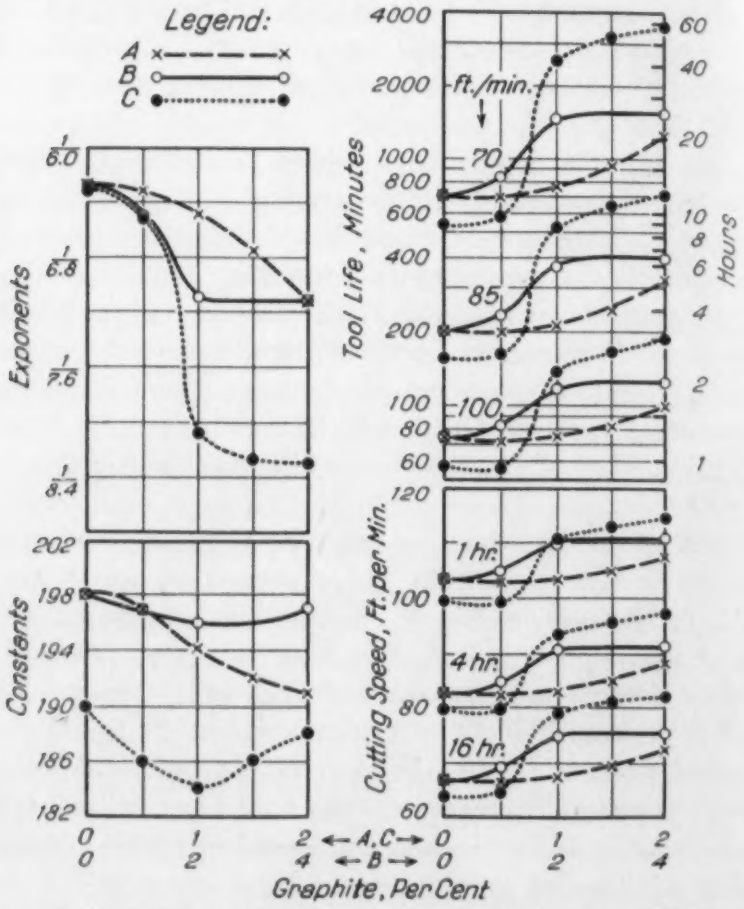


Fig. 9—Graphic Representation of the Influence of Various Amounts of Colloidal Graphite Suspended in Three Cutting Fluids.
The *Dashed Line*, Scale A, Represents "Aquadag" Added to a 16 to 1 Emulsion A, Table V.
The *Solid Line*, Scale B, Represents "Oildag" Added to the Soluble Oil Before Being Reduced With 16 Parts of Water.
The *Dotted Line*, Scale C, Represents "Oildag" Added to a Light Mineral Oil.

graphite up to a quantity of 0.0125 pound per gallon of emulsion. The cutting speeds for each of three values of tool life of 1 hour, 4 hours, and 16 hours are shown as a function of the quantity of graphite used in the emulsion. For each of the tool life values, there is an appreciable increase in cutting speed as the amount of graphite in the

Table VII

A Summary of the Tool Life-Cutting Speed Relation for Various Cutting Fluids with and without graphite, when turning an S.A.E. 3140 steel forging with 18-4-1 high speed steel B. The feed was 0.0125 inch per revolution, and the depth of cut was 0.100 inch. A ⅜-inch square section tool of the shape 8-14-6-6-6-15-3/64-R was used.

Cutting Fluid	Cutting Speed-Tool Life Equation	Cutting Speed for 20 Minutes	Cutting Speed for 2 Hours
D	$VT^{1/8.8}=178$	110	83
WB	$VT^{1/8.8}=207$	129	97
Emulsion A	$VT^{1/8.9}=198$	123	93
Emulsion A-½-A	$VT^{1/8.8}=197$	122	92
Emulsion A-1-A	$VT^{1/8.6}=194$	122	93
Emulsion A-1-½-A	$VT^{1/8.75}=192$	123	95
Emulsion A-2-A	$VT^{1/7.1}=191$	125	97
Emulsion A-1-0	$VT^{1/8.5}=197$	124	94
Emulsion A-2-0	$VT^{1/7.1}=196$	129	100
Emulsion A-4-0	$VT^{1/7.1}=197$	129	100
Emulsion B	$VT^{1/8.3}=192$	119	90
Emulsion B-2-0	$VT^{1/7.1}=192$	126	98
Emulsion C	$VT^{1/8.3}=189$	117	88
Emulsion C-2-0	$VT^{1/8.5}=183$	129	104
M	$VT^{1/8.3}=190$	118	89
M-½-0	$VT^{1/8.5}=186$	117	89
M-1-0	$VT^{1/8.1}=184$	127	102
M-1-½-0	$VT^{1/8.25}=186$	129	104
M-2-0	$VT^{1/8.3}=188$	131	106
S M	$VT^{1/8.9}=195$	126	97
S Cl M	$VT^{1/8.9}=195$	126	97

cutting fluid is increased up to 0.0125 pound per gallon of emulsion or 0.150 per cent by weight. This seems to be the minimum amount of graphite to give a maximum increase in cutting speed. For instance, on a 4-hour tool life, the cutting speed is increased from about 83 f.p.m. to 91 f.p.m. as graphite up to 0.0125 pound per gallon is added. At the upper right in Fig. 9 the tool life for cutting speeds of 70, 85, and 100 f.p.m. are given for each of the graphite contents. Again, an appreciable increase in tool life is obtained for all values of cutting speed as the amount of graphite in the emulsion is increased from 0 to 0.0125 pound per gallon. For the 70 f.p.m. speed, the tool life is increased approximately 100 per cent from about 710 minutes to 1500 minutes.

When the graphite is suspended in oil and added to the soluble oil before being reduced with water, as discussed above, the finish on the work is found to be greatly improved. In fact, the finish was equal in smoothness to that obtained by any of the oils. This emulsion containing graphite did not have the objectionable features of the emulsion to which graphite in water was added, inasmuch as the machine and work were left quite clean. When the surface dried, no graphite spots remained, the graphite apparently being carried away suspended in the oil. The use of colloidal graphite in this manner appears to have commercial possibilities.

The colloidal graphite in an oil carrier also was added to the two other types of soluble oils. The results of the experiments are given in Table VII under Emulsion B. This emulsion was made of 1 part type B soluble oil, in the ratio of 1 part oil to 16 parts of distilled water. When containing no graphite, the resulting equation was $VT^{1/6.3} = 192$. For Emulsion B-2-0, containing 0.150 per cent of graphite by weight, the resulting equation was $VT^{1/7.1} = 192$.

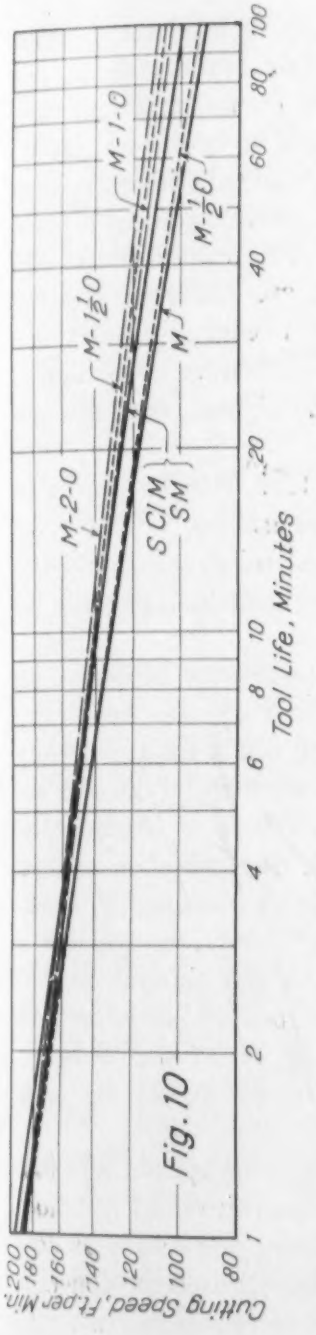
The reduction in the value of the exponent as the graphite is added shows that the curve becomes more horizontal. The constant, remaining the same, shows that the curve pivots about the cutting speed for a tool life of 1 minute. Table VII shows an appreciable increase in cutting speed for both the 20-minute and the 2-hour tool life values.

Emulsion C, Table VII, is similar to Emulsion B, except that the third type of soluble oil was used. Emulsion C-2-0 contains 0.150 per cent colloidal graphite by weight. The difference between the equations for the two emulsions shows a reduction in the value of the exponent from 1/6.3 to 1/8.5 and a slight reduction in the value of the constant. An appreciable increase in cutting speed is shown for both the 20-minute and the 2-hour tool life values.

It was found that when soluble oil B was used, the suspension of the colloidal graphite was very poor. Even while running the tests, an appreciable amount of the graphite was thrown out of the emulsion. When using soluble oil C in the form of an emulsion containing the graphite, there was evidence that over a period of two or three weeks a considerable amount of graphite would be lost from the emulsion. These facts are mentioned, inasmuch as many statements have been heard to the effect that graphite in various types of emulsions has been used with little success. Emulsion A, being more stable, indicates that there is a possibility of using graphite to advantage in emulsions, inasmuch as both the tool life and finish are improved.

Influence of Colloidal Graphite in Mineral Oil

Additional cutting speed-tool life tests were carried out on the S.A.E. 3140 steel with the "Standard" shape of tool operating at a feed of 0.0125 inch and a depth of 0.100 inch. A plain light mineral oil, a sulphurized mineral oil, and a sulpho-chlorinated mineral oil were used, together with the plain mineral oil plus various quantities of colloidal graphite. The graphite suspended in an oil carrier was



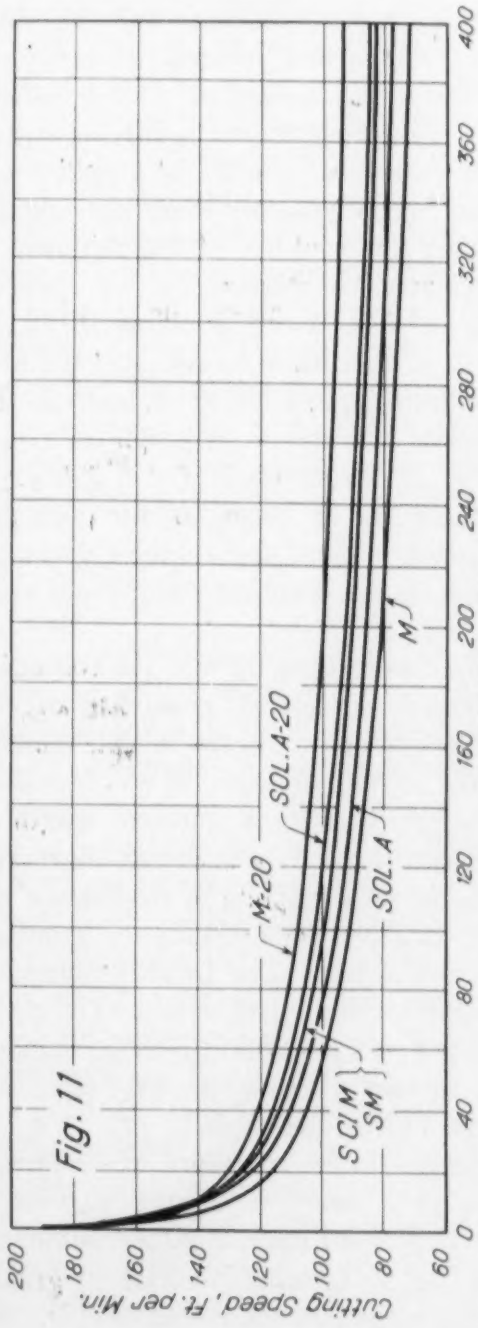


Fig. 10—Cutting Speed-Tool Life Curves Plotted on Log-Log Paper for Plain Mineral Oil (M), Sulphurized Mineral Oil (SCIM + SM), and Mineral Oil Containing Various Quantities of Colloidal Graphite. S.A.E. 3140 Steel Annealed and Normalized was Turned with Tools *B* of 18-4-1 High Speed Steel Ground to the "Standard" Shape. The Feed was 0.0125 In. and the Depth of Cut 0.100 In.

Fig. 11—The Cutting Speed-Tool Life Curves of Fig. 10 Plotted on Cartesian Co-ordinates. The Dotted Line Curves Represent the Influence of Various Amounts of Colloidal Graphite in a Mineral Oil on the Constants, Exponents, Tool-Life, and Cutting Speed. Data from Table VII.

added in percentages by weight of 0.038, 0.076, 0.114, and 0.153, in the oils indicated respectively as M-½-0, M-1-0, M-1-½-0, and M-2-0 in Table VII. All cutting speed-tool life curves for the oils are plotted in Fig. 10.

It is shown that the data for the sulpho-chlorinated mineral oil and the sulphurized mineral oil are identical, resulting in one curve, which is the highest of all for values of tool life less than 5 minutes. The lowest curve is for the straight light mineral oil M. As various quantities of colloidal graphite are added, the curves are elevated and become slightly more horizontal, pivoting about a point corresponding to a tool life of 1½ minutes. For values of tool life above 5 minutes, the highest cutting speeds are obtained with the mineral oil M-2-0, which contains 0.153 per cent by weight of graphite. It is interesting to note that the lowest curve in the figure, obtained with the plain mineral oil, becomes the highest curve through the addition of this amount of graphite.

Values of cutting speed for a 2-hour tool life are shown in Table VII as being 89 f.p.m. for the plain mineral oil, 97 f.p.m. for the sulphurized mineral and sulpho-chlorinated mineral oil, and 106 for the mineral oil containing 0.153 per cent colloidal graphite by weight.

Attempts were made to add the colloidal graphite suspended in oil to a sulphurized-base oil consisting of about 3½ per cent fatty oil, ½ per cent sulphur, and the balance mineral oil, having a viscosity of about 160 Saybolt seconds. It was found that the graphite did not remain in suspension for a sufficient length of time to obtain satisfactory performance. It was found, however, that the plain mineral oil kept the colloidal graphite in suspension very satisfactorily, showing only 2 to 3 per cent settling of graphite after standing for a period of three weeks. The finish produced by the mineral oil containing graphite was the best of all. The oil appeared black, but was clean to work with, inasmuch as in running from the work or machine it carried the graphite with it in suspension, leaving none on the surface or on the chips.

The changes in the constants, exponents, cutting speeds, and tool life values as a function of the various quantities of colloidal graphite carried in the mineral oil are summarized graphically as dotted lines in Fig. 9. A small addition of graphite causes the constant to fall off to a minimum for the oil M-1-0. It increases thereafter to a satisfactory maximum for M-2-0. The exponent of the equation is highest, producing the steepest curve, when no graphite is contained in the mineral oil, as shown at the upper left in Fig. 9. With the addition of small quantities of graphite, the exponent drops rapidly to a minimum of 1/8.3 for the mineral oil M-1-½-0, after which no

appreciable reduction is obtained with further additions of graphite. Because of the rise of the constant for the M-2-0 oil, it is felt that the graphite content of 0.153 in per cent by weight, corresponding to that of the oil M-2-0, should be the minimum amount to be used.

At the lower right in Fig. 9 is shown the values of cutting speed for each tool life of 1 hour, 4 hours, and 16 hours as the content of graphite is increased. The overall increase is appreciable, averaging approximately 20 per cent. The tool life for a constant cutting speed, as shown at the upper right in Fig. 9, also increases very favorably as the oil contains quantities of graphite in excess of that of oil M-1-0. The increase in tool life obtained by the greatest amount of colloidal graphite in oil averages from 400 to 600 per cent, whereas, the increase in cutting speed using the colloidal graphite suspended in oil in an emulsion produced about 100 per cent increase.

Summary

In summarizing the above experiments, those curves considered most significant are replotted on the modified log-log scale in Fig. 12. The equations are summarized in Table VI. The lowest curve is obtained when cutting dry, the highest curve for a tool life value in excess of 13 minutes is obtained with the light mineral oil containing 0.153 per cent colloidal graphite by weight. The other curves are intermediate. It is interesting to note that, for a tool life below 13 minutes, the highest values of cutting speed are obtained for any given tool life with the borax water WB. The curve obtained by the use of the 16 to 1 emulsion, Emulsion A, containing 0.150 per cent colloidal graphite by weight suspended in oil, is consistently higher than the corresponding curve for the sulphurized oils. This figure shows clearly that both the slope, which affects the exponent, and the vertical position on the scale, which affects the constant, are affected by the use of the different types of cutting fluids.

Some of the curves of Fig. 12 have been replotted on Cartesian co-ordinates in Fig. 11 to make the results more conveniently legible.

Several recent surveys regarding the use of tools and cutting fluids show wide variations in commercial practice. There appears to be great opportunities for commercial savings in production by using that type and shape of tool, that proportion of the cut, that heat treated condition of the material, and that cutting fluid which will produce the best quality and quantity of work. A careful

analysis will show that the cost of changing any one item may not be significant when compared with the final cost of the work. From the information available regarding the various elements, it is possible to predict, for set-up purposes, with very close accuracy those conditions which will lead to the greatest production at the least cost. One is apt to be misled from the results of commercial tests,

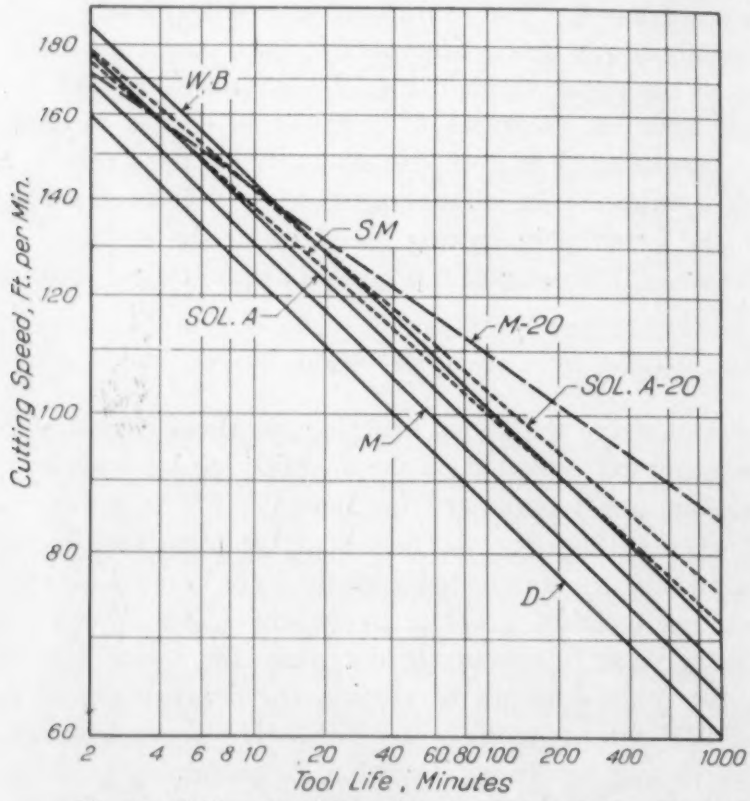


Fig. 12—Cutting Speed-Tool Life Curves for Various Types of Cutting Fluids Plotted on Modified Log-Log Co-ordinates, When Turning S.A.E. 3140 Steel Normalized and Annealed, with Tools *B* of the 18-4-1 Type High Speed Steel Ground to the "Standard" Shape. The Feed was 0.0125 Inch and the Depth of Cut 0.100 Inch.

inasmuch as performance under one condition might be different from a corresponding performance under some other condition. For this reason, it is strongly recommended that, as far as possible, the desirable operating conditions be decided upon, such as the time between grinds of a tool or the given cutting speed, before obtaining comparative data. If the time between grinds is allowed to change, this factor in itself might account for a decided change in performance. These variations are due to a change in exponent and constant in the cutting speed-tool life equation as influenced by any one of the many variables involved.

In one specific case, the production on a multiple spindle automatic screw machine was increased 12 per cent by changing cutting fluids which allowed the cutting speed to be increased to maintain the same tool life. The first plain mineral oil cost 16 cents per gallon and the new sulphurized-base oil cost 24 cents per gallon. Considering the direct labor cost and machine overhead, the 12 per cent increase in production was obtained by a 1.65 per cent increase in total cost. Similarly, the production of the screw machine might be increased by prolonging the life of the tools, while operating at the same speed, through changing any of the variables involved. This would require less tool grinding, resulting in less idle machine time for changing tools. Similar results may be obtained by changing any other variable involved.

Conclusions

The data presented above show that a change in any one of numerous operating conditions might change the slope and height of the cutting speed-tool life curve and produce favorable or unfavorable conditions. Specific conclusions are as follows:

1. A change in tool shape, by altering the nose radius, side-cutting angle, side-rake angle, or back-rake angle, will change both the slope of the cutting speed-tool life curve and its vertical position on the scale.

2. The cutting speed-tool life curve may be changed in slope or in elevation on the scale by substituting one brand of high speed steel for another, other conditions remaining the same. The order of performance will change as cutting conditions are changed so that one tool may be inferior on one job but superior on another.

3. The analysis of the material cut influences the nature of the cutting speed-tool life curve. Different structures produced by heat treating also produce similar changes.

4. For a given size and shape of cut, using a single tool material and test log, each cutting fluid produces a characteristic equation representing the relation between cutting speed and tool life. Both the exponent and constant of the equation may be varied.

5. For a given area of cut, other factors remaining the same, the results obtained with a shallow thick cut differ from those of the deep thin cut.

6. The use of oils on the shallow thick cut caused the log-log

curves to become steeper, whereas when used on the deep thin cut, the curves become more horizontal, indicating opposite tendencies.

7. In all tests reported, the same exponent in the cutting speed-tool life equation is obtained when cutting dry and with aqueous solutions and emulsions, but characteristic values of the constant are obtained.

8. The addition to an emulsion of colloidal graphite suspended in water produces slightly favorable tool life values but inferior finish. The work, operator, and machine were left extremely dirty, however.

9. When colloidal graphite suspended in oil is added to the soluble oil before reduced with water to make an emulsion, the slope of the cutting speed-tool life curve with the horizontal is reduced, while the constant remains practically the same. When colloidal graphite of not less than 0.150 per cent by weight is added to the emulsion, the cutting speed for a given tool life is increased about 10 per cent and the tool life for a given cutting speed is increased about 100 per cent. This emulsion was clean and proved to be very satisfactory as a cutting fluid.

For commercial use it seems desirable that the colloidal graphite carried in oil be added to the soluble oil at the time of its manufacture. Some types of soluble oils proved to be poor carriers of the graphite.

10. When colloidal graphite is added in increased quantities to a plain mineral oil, the resulting cutting speed-tool life curves becomes more horizontal, showing the exponent to be reduced with a very slight change in the value of the constant. Maximum benefits in cutting speed or tool life are obtained when the per cent of colloidal graphite by weight in the mineral oil is 0.153. For a given tool life, an increase in cutting speed under these conditions averages 20 per cent. For a given cutting speed, the tool life increases 400 to 600 per cent. The addition of the colloidal graphite to the mineral oil darkened the color of the oil, but it did not prove to be objectionable, as the machine and work were left clean as the oil ran off. Only about 3 per cent of the colloidal graphite was found to settle out of the oil on standing for a period of three weeks.

11. When turning S.A.E. 3140 normalized and annealed with 18-4-1 high speed steel tools ground to the "Standard" shape of 8-14-6-6-6-15-3/64R, with a feed of 0.0125 inch and a depth of cut 0.100 inch, Fig. 10, the order of the cutting fluids from the lowest to

the highest, giving the cutting speed for a 2-hour tool life (in parenthesis), is as follows:

a) Dry cutting, the lowest (83)
b) Plain mineral oil (89)
c) 1-16 emulsion, Emulsion A (93)
d) Sulphurized mineral and sulpho-chlorinated mineral (97)
e) 1-16 emulsion containing 0.150 per cent by weight of colloidal graphite (100)
f) Mineral oil, containing 0.153 per cent colloidal graphite by weight, highest (106)

This represents an overall increase of 28 per cent for the 2-hour tool life.

12. For short values of tool life, water plus borax or plain water gives the greatest cutting speed for any tool life below 13 minutes.

Acknowledgments

The authors are grateful to G. C. Riegel, Chief Metallurgist of the Caterpillar Tractor Company, through whom the Republic Steel Company generously supplied the S.A.E. 2345 steel used in the first part of the paper.

Acknowledgment is made to C. N. Rix of Michigan State College and W. J. Starr of Southwestern (Louisiana) University, who, as graduate students at the University of Michigan, ran the tests on the S.A.E. 2345 steel.

DISCUSSION

Written Discussion: By E. A. Bodine, Acheson Colloids Corp., Port Huron, Mich.

The results of Professor Boston's efforts form a firm foundation and an indication as to the approach to be made in further investigation of the cutting fluids problem. Professor Boston has considerably advanced the art of machining as a result of his extensive research in this field, but much more work of a practical nature, embracing tests in production plants, must be performed before machining can begin to approximate a science. In this connection, each machining job must be approached as an individual operation and the best conditions determined by trial and error.

The paper indicates the utility of colloidal graphite as an adjunct for cutting fluids, be they of the emulsion or plain mineral oil type. There is one point in the paper which might well be emphasized, i.e., the correct proportion

of colloidal graphite to use. The paper states that optimum results were obtained with 0.150 per cent by weight of colloidal graphite added to the soluble oil of the emulsion, and with 0.153 per cent by weight of colloidal graphite added to plain mineral oil. It would probably simplify matters if it were stated that these figures are equivalent to two fluid ounces of the concentrated commercial product, "Oildag," per gallon of cutting fluid.

Although the speeds used in these tests are not of the highest, they were selected, apparently as fixed factors suitable for the purpose. Operators, desiring to apply the results of this paper, should do so by analogy, even though the cutting fluid which shows best at 100 to 200 feet per minute may not be so good at higher speeds. As has been previously stated, experience indicates that each machining operation should be observed as an individual one and the proper cutting fluid determined by practical test.

The effect of cutting fluid cost should be studied in terms of increased production and betterment of the machined surface rather than in terms of the initial cost of the cutting fluid. In this connection, the use of a colloidal graphite cutting fluid can be justified economically by the computations below which are based upon Fig. 12 of the paper. It might be well to state here that the cost of the colloidal graphite as indicated is based on medium quantity purchases and is subject to revision downward on larger orders.

For a constant tool life of 300 minutes (as seen from Fig. 12) the cutting speed for the plain mineral oil is 77 feet per minute; for the sulphurized oil 86 feet per minute; and for the mineral oil plus colloidal graphite (M-2-0) it is 96 feet per minute. The increase in speed or production for the sulphurized oil over the plain mineral is approximately 12 per cent and for the mineral oil plus colloidal graphite over the plain oil, 25 per cent. The mineral oil plus the necessary colloidal graphite (2 ounces of concentrated colloidal graphite in oil per gallon) cost 35 cents. Assuming, as in Professor Boston's report, the use of these oils on an automatic screw machine in which one gallon of cutting fluid is added per hour, we have the following:

	Plain Oil	Sulphurized Oil	Mineral Oil Plus Colloidal Graphite
Direct Labor	$ .40	$ .40	$ .40
Tool Cost (Material and Grinding)	.20	.20	.20
Machine overhead	4.00	4.00	4.00
Cutting fluid cost (plain oil)	.16	.24	.16
Colloidal graphite	.....	.....	.19
Total	$4.76	$4.84	$4.95
Increased cost over that of plain oil	.....	$0.08	$0.19
	.....	1.65%	3.9%
Increased production over that of plain oil	.....	12%	25%

It might be well, also, to emphasize the fact that colloidal electric furnace graphite is abrasive-free, inert chemically, and of a particle size that makes it, for all practical purposes, the equivalent of a substance in true solution. Being inert, of course, colloidal graphite does not promote corrosion. It would seem that colloidal graphite possesses many possibilities in the cutting fluid field and that a wider practical use of the same in this connection is worthy of serious consideration.

Oral Discussion

W. H. OLDACRE:[1] I deeply regret that limited time prevented an adequate written discussion of this fine paper. We have had occasion to congratulate Professor Boston and his associates on their special and time-taking work, and we want to continue to express our full appreciation. I do want to ask those who are in attendance here to take a copy of this paper home with you, and some time when you have an hour to spare give it a little careful consideration. When you have done that you will appreciate more fully the complexity of the machining operation, and I think you will understand that it will require careful study and special thought to reach definite conclusions. We find that most people in the factories are given to jumping to conclusions when it comes to their consideration of cutting fluids, and all we are asking is that you take a little care and a little thought and give consideration to the engineer who is honestly trying to give you a good service in the cutting fluid field. I know that Professor Boston is going to continue this work. He has a very extensive program outlined, and we in our organization are looking forward to future reports of this type.

GEORGE BOUVIER:[2] We who use various machining processes have no doubt applied some of the research data that Professor Boston and his associates are responsible for. I feel that we are going to become more dependent upon that work. If we are to advance the art of machining, we must stop trying to do it in the old practical cut and try way that was generally followed ten or twenty years ago, and take more advantage of university work. We should be very appreciative of what the university investigators have accomplished and I dislike to admit that we have not in the past applied the new knowledge to the extent we should in the future. In looking at the various curves shown by the authors we note that they appear to be very close to each other. I am aware that these curves are plotted from the mean values of many tests. Possibly if we were to see the distribution of the different test values as obtained, we might find that the area enclosed by a maximum curve and a minimum curve through the random variations, would overlap the plotted results of a different test.

The degree to which this is true would influence somewhat how we would interpret the curves, and apply the data. I should like to ask the authors to explain what degree of accuracy can be expected of the curves, of course bearing in mind the conditions of the test.

Closure by Authors

The authors greatly appreciate the interest shown in this paper as manifest by the discussion in the limited time available.

The results of the several experiments reported on in this paper were intended to show the marked influence of any single variable on the cutting speed-tool life curve. It is recognized, however, that were any of these series of experiments run under other conditions such as with different tool material

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[1]Director of Research and Engineering, D. A. Stuart & Co., Chicago.
[2]Western Electric Co., Hawthorne Station, Chicago.

or shape, different size of cut, or different material cut, results of a different ratio and perhaps of a different order might be obtained.

Mr. Oldacre's remarks relative to the drawing of general conclusions from these specific tests are, therefore, appropriate. It is believed that one cutting tool material or one cutting fluid might prove to be superior in one case but decidedly inferior under another set of conditions. Just what happens when metal is cut is still a matter of debate, particularly when metals are cut with tools of different shape and with cutting fluids of different types. The manufacturer, therefore, is fortunate to have competent engineers to call on for advice based on practical experience. Careful experimental work of a much more extensive nature is needed in order that the factors involved in tool life, power, and finish can be explained separately or correlated. That cutting fluid, for instance, best suited for heavy duty work may be quite unsuited for finishing work where surface finish and accuracy are of paramount importance.

It is rather difficult to answer Mr. Bouvier's question concerning the accuracy of the various tool life-cutting speed curves. Each of these curves has been drawn through from eight to twelve points determined experimentally. If any one of these points does not fall reasonably close on the line, it is checked. It is believed that no point considered reliable differs from the straight line values by more than 1 per cent of that cutting speed.

Mr. Bodine has brought out clearly the relation between the initial cost of the cutting fluid and the final cost per piece based on the curves of Fig. 12 in which the performance of various types of cutting fluids is compared. This emphasizes the often overlooked fact that an apparently expensive cutting fluid may become the cheapest, even on roughing work, by virtue of its increased production.

PHYSICAL PROPERTIES OF METALS AS AFFECTED BY CONDITIONS OF AMMONIA SYNTHESIS

By H. L. Maxwell

Abstract

The chemical processes developed during the last ten to fifteen years have required new and improved materials to withstand the conditions of temperature and pressure being employed. This applies particularly in hydrogenation and synthesis processes. The problems to be considered in the selection of materials for such applications as high pressure, hydrogenation and synthesis ammonia are tensile strength, ductility and shock resistance at high temperatures, resistance to hydrogen attack and creep under long continued high stresses. The work reported in the present paper was undertaken in order to gain further information on metals having the desired properties required for these operations. The results show that deoxidized copper and copper alloys are more resistant to high temperature, high pressure hydrogen-nitrogen mixtures than similar alloys containing oxide. Plain carbon steel and also low chrome-nickel alloys are severely embrittled at temperatures up to 500 degrees Cent. in contact with 3:1 hydrogen-nitrogen mixtures at 1000 atmospheres pressure. The chrome-tungsten, chrome-molybdenum, and chrome-vanadium steels show increased resistance to gas attack under these same conditions for intervals up to 1535 hours.

THE development of a new chemical process cannot be said to be complete until equipment, usually constructed of metals, has been developed and is capable of carrying out the operation safely and producing a commercially salable product at a profit and with a reasonable degree of permanence as regards the equipment.

The problem of development and selection of metals for high temperature, high pressure equipment is relatively new. There has been some experience in hydrogenation equipment which operates under pressure and temperature. The nitriding reaction at atmospheric and also increased pressures has also been studied extensively.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The author, Dr. H. L. Maxwell, is Metallurgist, Engineering Department, E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware. Manuscript received June 1, 1935.

It has been concluded from the investigations that have been made to date that while there is a relationship between hydrogenation, the nitriding reaction and ammonia synthesis in their effect on methods used in construction of equipment, in many respects the effects of these three processes on metals are distinctly different.

When a mixture of hydrogen and nitrogen in a 3:1 ratio is brought in contact with a suitable catalyst with temperature and pressure condition of up to 500 degrees Cent. (930 degrees Fahr.) and 15,000 pounds, respectively, a large proportion of the constituent gases is converted into anhydrous ammonia, NH_3. Although there are numerous references in the literature on the resistance of metals to the process condition found in the high pressure hydrogenation there is but little published information on materials of construction for use in ammonia synthesis equipment employed under the temperature and pressure conditions as described above and which are particularly corrosive to many metals. It will not be the purpose of this present paper to review the history of metal problems of either hydrogenation or nitriding except to the extent that these references may have a bearing on the specific problem of materials as affected under conditions of ammonia synthesis. The present discussion will be confined to the effect of the conditions of ammonia synthesis on the physical properties of metals.

The metals and alloys included in the present tests may be grouped into three general classifications:

(1) Copper and copper alloys
(2) S.A.E. steels and irons (Low alloyed steels and irons)
(3) Nickel-chromium-iron alloys.

For convenience, these three sub-divisions will be maintained in the description of the experimental parts and also in considering the conclusions.

General

All of the test bars were 1.5 by 0.5 by 12 inch with a machined section of 1 by 0.5 by 6 inches in the center leaving a 1.5 inch wide section about 3 inches long for the tensile testing machine grips. All test bars were annealed 20 hours at 500 degrees Cent. (930 degrees Fahr.) before test and later exposed in duplicate to process conditions for time intervals of 162 hours, 645 hours, and 1535 hours.

Copper and Copper Alloys

The limited amount of previous work done on the effect of hydrogen-nitrogen mixtures on copper might be supplemented by reference to the work of other investigators who studied the reaction of copper to the effects of gases containing hydrogen under less drastic conditions of temperature and pressure than that encountered in the synthesis of ammonia.

In studying the action of reducing gases on hot solid copper, N. B. Pilling[1] subjected hot copper to a stream of mixed gas rich in hydrogen and showed a reducing effect. W. H. Bassett and J. C. Bradley,[2] in making further studies, treated hot copper with illuminating gas containing 38 per cent hydrogen. The results indicated that the hydrogen, which was the most readily diffused gas, reacted essentially the same in all cases. The results of Smith and Hayward[3] also support these findings.

In a series of three papers, L. L. Wyman[4] reported the results of extensive work on embrittlement of copper. The principal two of the five conclusions reached were:

> The rate of oxygen penetration into "pure" copper decreases markedly below 800 degrees Cent. (1470 degrees Fahr.) The rate of hydrogen penetration into oxygen-bearing copper decreases markedly below 700 degrees Cent. (1290 degrees Fahr.).
>
> The embrittlement due to pure hydrogen is of the same order of magnitude as that caused by illuminating gas (Bassett and Bradley).

Although the foregoing review of previous work does not relate directly to conditions of ammonia synthesis it does serve to point out that hydrogen will diffuse into copper even at atmospheric pressure. In view of the low cost and workability of certain of the copper alloys, these materials were found of sufficient promise to warrant including in the materials to be studied in the present investigation.

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[1]N. B. Pilling, *Journal*, Franklin Institute, Vol. 186, 1918, p. 373.

[2]W. H. Bassett and J. C. Bradley, "Action of Reducing Gases on Heated Copper," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 73, 1926, p. 755.

[3]C. S. Smith and C. R. Hayward, *Journal*, Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, Vol. 36, 1926, p. 211.

[4]L. L. Wyman, "Copper Embrittlement," American Institute of Mining and Metallurgical Engineers, Preprint 1931; Part II, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 104, 1933, p. 141; Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, Vol. 3, 1934, p. 205-13.

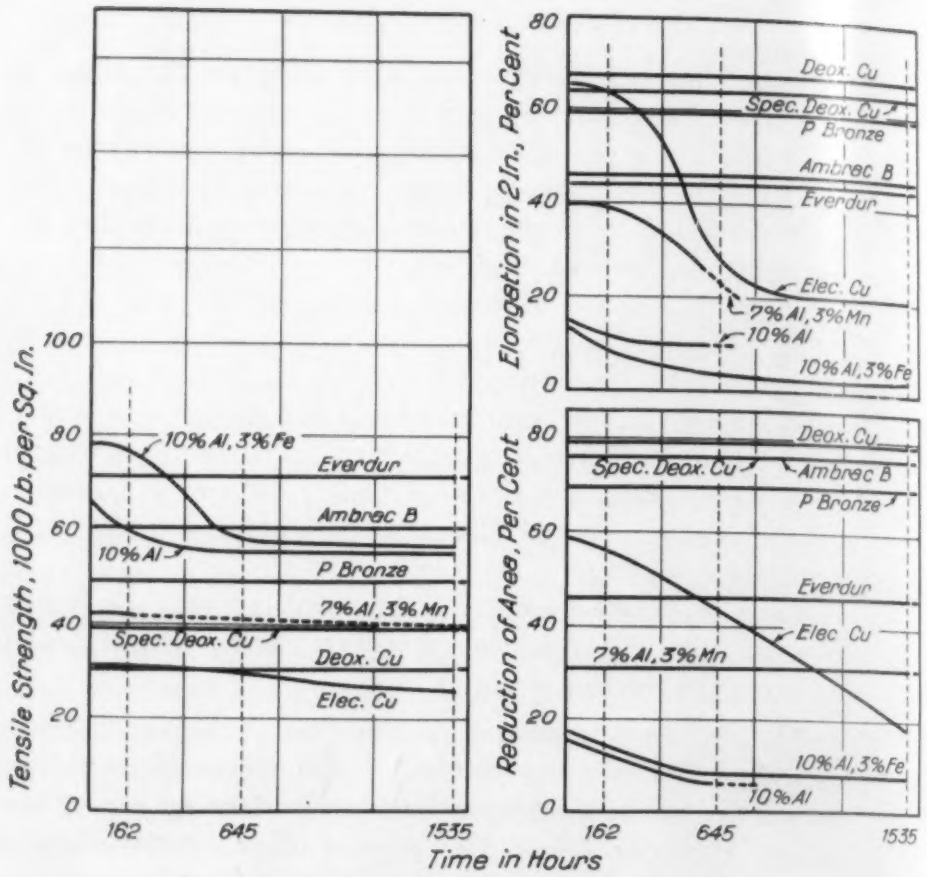

Fig. 1—Physical Properties of Copper and Copper Alloys.

Experimental

The compositions of the copper alloys used in the present tests are given in Table I.

Table I
Copper and Copper Alloys

Name	Approximate Compositions	Condition
Electrolytic Copper	Cu 99.9	Rolled
Deoxidized Copper	Cu 99.1 + .03 P	Rolled
Special Deoxidized Copper	Cu 99.0 + .5 P	Rolled
Tin Bronze	Cu 96.0; Sn 4	Rolled
Everdur	Cu 95; Si 3.0; Mn 1.1	Rolled
Ambrac B	Cu 65.0; Zn 5.0; Ni 30.0	Rolled
Aluminum Bronze 1	Cu 90; Al 10	Cast
Aluminum Bronze 2	Cu 87; Al 10; Fe 3	Cast
Aluminum Bronze 3	Cu 90; Al 7; Mn 3	Cast

All test bars were annealed 20 hours at 500 degrees Cent. (930 degrees Fahr.) before exposure. Duplicate bars of each of the com-

positions shown in Table I were exposed at varying time intervals as determined by convenience of operations. The times of exposure were 162, 645, and 1535 hours. The test bars were exposed to 3:1 ratio of hydrogen-nitrogen gas mixture at 1000 atmospheres pressure and at temperatures up to 500 degrees Cent. (930 degrees Fahr.).

The curves in Fig. 1 show the physical properties of the test bars after exposure in the hot gases for the time intervals indicated.

Discussion of Results

Microscopic examination of the specimen of electrolytic copper after test exposure revealed definite evidence of hydrogen attack at the grain boundaries. The extent of the hydrogen attack at the grain boundaries was sufficient to account for the decrease in physical properties of the test bars after exposure to gas. In several of the oxide-rich areas the reaction between the hydrogen and copper oxide was sufficient to form blisters ¼ inch below the surface of the copper test bar. This is probably due to the fact that the newly formed water vapor was not able to diffuse as readily as the hydrogen which formed it.

In the case of the three aluminum bronzes there is evidence of a gradual disintegration of the metal surface as a result of exposure to hydrogen and nitrogen at high temperature and pressure. This effect, which is indicated to be an interaction between aluminum and nitrogen, will be made the subject of a separate detailed study. The surface layers of the aluminum bronze test bars were depleted in aluminum.

The remainder of the copper and copper alloy test bars appeared to be unaffected.

Conclusion

It is concluded that when copper and copper alloys are exposed to hydrogen-nitrogen mixture in 3:1 ratio at 15,000 pounds pressure and temperatures up to 500 degrees Cent. (930 degrees Fahr.), the following conditions hold:

1. The effect of the hydrogen in the hydrogen-nitrogen mixture is greater than that of the nitrogen on any of the high copper aluminum-free alloys studied.
2. Deoxidized copper and copper alloys will retain their physical properties markedly better than similar alloys containing free oxide.

3. High copper alloys containing aluminum undergo a gradual deterioration, probably as a result of interaction between aluminum and nitrogen and, with long exposure, a depletion of the aluminum in the alloy on the surface results.

S.A.E. Steels and Irons

There are only a few references of published work on the resistance of ferrous metals to condition of ammonia synthesis at both the higher temperatures and pressures. The majority of the published data relate to different conditions of pressure and temperature and for this reason cannot logically be correlated with the results obtained in the present study. Therefore reference will be made to only a few.

Vanick[5] and collaborators working at 500 degrees Cent. (930 degrees Fahr.) and using the low pressure of 100 atmospheres, determined that a steel containing 2.25 per cent Cr, and not more than 0.30 per cent carbon, with or without vanadium, was resistant to these process conditions.

Earlier investigators have shown by means of tests under a wide variety of conditions of temperature and pressure that chromium steels with low carbon are, in general, more resistant to attack by hydrogen-nitrogen than are steels without chromium. It has been found by experience that when the results of some of the low pressure or lower temperature tests are applied to the higher temperatures and pressure process conditions the outcome is failure of the part.

A 3:1 hydrogen-nitrogen gas mixture was employed by Kosting,[6] in testing the resistance of chromium-tungsten steels to these gases. A steel containing 2.85 per cent tungsten was not attacked while one containing 0.81 per cent tungsten was attacked. The gas was compressed over water and probably contained sufficient water vapor to influence the results, to some degree. The test conditions approximated 300 degrees Cent. (570 degrees Fahr.) and 600 atmospheres pressure.

In the early experiments of Haber and Bosch[7] it was found

[5]J. S. Vanick, W. W. de Soeshnikoff and J. G. Thompson, "Deterioration of Steels in the Synthesis of Ammonia," Bureau of Standards Bulletin No. 361.

[6]P. R. Kosting, "Deterioration of Chromium-Tungsten Steels in Ammonia Gas," *Metals and Alloys*, Vol. 5, No. 3, March 1934, p. 54-56.

[7]Haber and Bosch, *Chemical Fabrik*, Vol. 6, 1933, p. 127.

that ordinary carbon steels were severely attacked by hot hydrogen under pressure.

In reviewing the data of various investigators who had worked with hydrogen at high temperature and pressure, it is observed that practically all are agreed that ingot iron and plain carbon steels are definitely attacked by hydrogen at 400 degrees Cent. (650 degrees Fahr.) under atmospheric or increased pressure.

It was shown by E. D. Campbell[8] that carbon could be transferred from a higher to a lower carbon steel specimen through the medium of a hydrogen atmosphere. This was followed by a paper Campbell, Fink and Ross,[9] where it was demonstrated that hydrogen could be used to transfer carbon quantitatively from a higher to a lower carbon-iron alloy. This was apparently made possible by the formation of an equivalent amount of hydrocarbon.

There was indication from the author's previous work that plain carbon and low alloy steels are acted upon by both the hydrogen and nitrogen when exposed to ammonia synthesis conditions. In order to determine the effect of these conditions on representative low alloy steels it was decided to expose test bars in a converter and determine the influence of long exposure on the physical properties of the metals.

Experimental

The following metals were selected as typical of iron and the low alloy steels:

Ingot Iron; the following S.A.E. steels, 1012, 1045, 2315, 3115, 4130, 5120, 6120 and 7260.

Test bars were made of all of these metals and exposed to process conditions of ammonia synthesis as described. Duplicate bars were removed from test after intervals of 162, 645 and 1535 hours.

The results of the physical tests on the exposed bars are shown in Fig. 2.

Discussion of Results

Microscopic examination of the iron and low alloy steel test

[8]E. D. Campbell, "The Decarburization of Steel with Hydrogen," *Journal*, Iron and Steel Institute, 1919, p. 407.

[9]E. D. Campbell, W. L. Fink and J. F. Ross, "The Iron-Carbide Equilibrium in Dry Hydrogen at 950 Degrees Cent.," *Journal*, Iron and Steel Institute, Vol. 108, No. 2, 1923, p. 173.

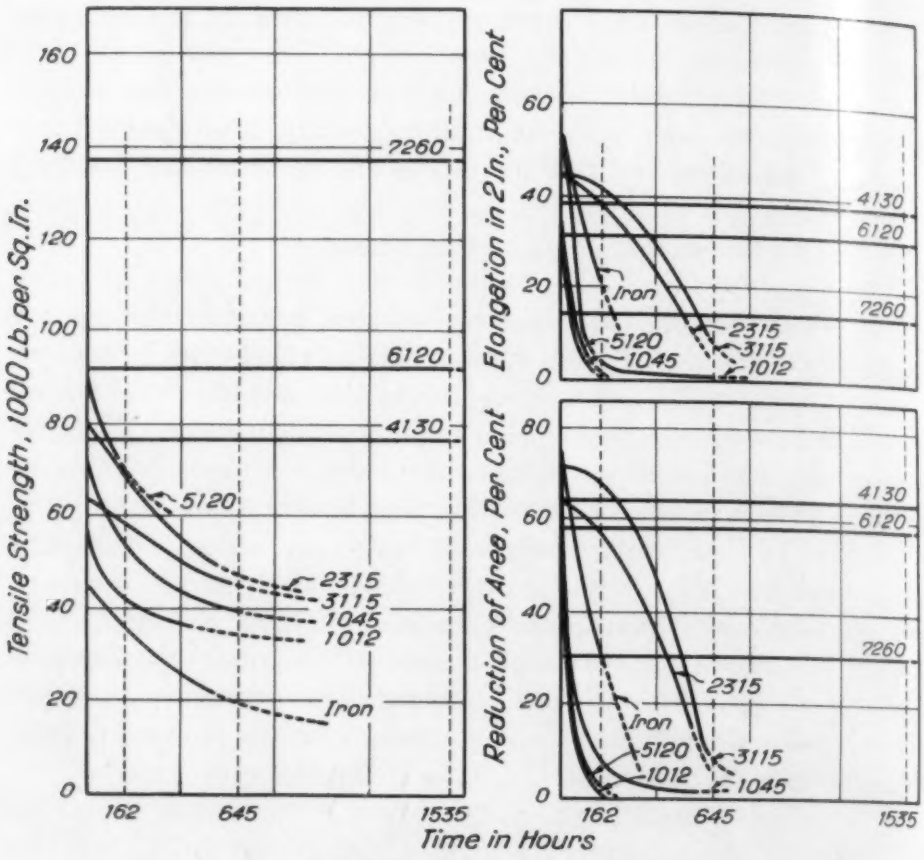

Fig. 2—Physical Properties of S.A.E. Steels and Iron.

bars after exposure showed that all but three were embrittled and that there was evidence of nitrides. The plain carbon steels were decarburized on the surface.

In discussing the preliminary results of this work at the regional meeting at Pennsylvania State College in May, 1934, the writer pointed out that the examination of the test bars lead to this conclusion: that the reaction of these materials under ammonia synthesis conditions is primarily one of decarburization and embrittlement, and only secondarily one of nitride formation. Both of these are side reactions as described subsequently.

If the equation—

$$3H_2 + N_2 = 2NH_3$$

is written it is clear that high pressure tends to promote the reaction from left to right. When hydrogen-nitrogen mixture in 3:1 ratio is under temperature and pressure conditions favorable for ammonia

synthesis, there are several side reactions also likely to take place. The principal side reactions are:

$$(1)\quad Fe_3C + 2H_2 \rightarrow CH_4 + 3Fe$$
$$(2)\quad NH_3 + \text{metals} \rightarrow \text{nitrides of metals}$$

The decarburizing reaction (1) is accelerated with increasing temperature and pressure. The nitriding reaction (2) is influenced by temperature, but to a less degree by variation of pressure.

It is now believed to be well established experimentally that the effect of high pressure hydrogen and nitrogen on carbon steel is mainly decarburizing in action. It might be safe to postulate that Fe_3C, being a metastable compound, would tend to break down rather rapidly under the proper temperature and pressure conditions. It appears equally true that the carbide-forming elements that form stable carbides and in turn exert a stabilizing influence on the Fe_3C contained in double carbides, are the best probabilities as alloying elements in building alloys with maximum resistance to hydrogen attack.

Conclusions

Iron and plain carbon steels undergo marked loss of physical properties on exposure to 3:1 hydrogen-nitrogen moisture under the test conditions.

Vanadium, molybdenum and tungsten appear to have a profound influence in stabilizing carbide against the action of hydrogen-nitrogen at high temperature and pressure.

High Nickel-Chromium Ferrous Alloys

There is need in certain parts of process equipment, for a metal that maintains its physical properties at higher temperatures and pressures than those already described. For these purposes it is necessary to employ alloys which have great resistance to hydrogen attack at high temperature and pressure and also a sufficient margin of safety in creep resistance to withstand occasional peaks of pressure and temperature in plant operation. A valuable contribution to the information on the influence of alloying elements in increasing creep resistance and related properties in metals at high temperatures is found in "Symposium on Effect of Temperature on the Properties of Metals" by R. W. Bailey, J. H. S. Dickinson, N. P. Inglis and

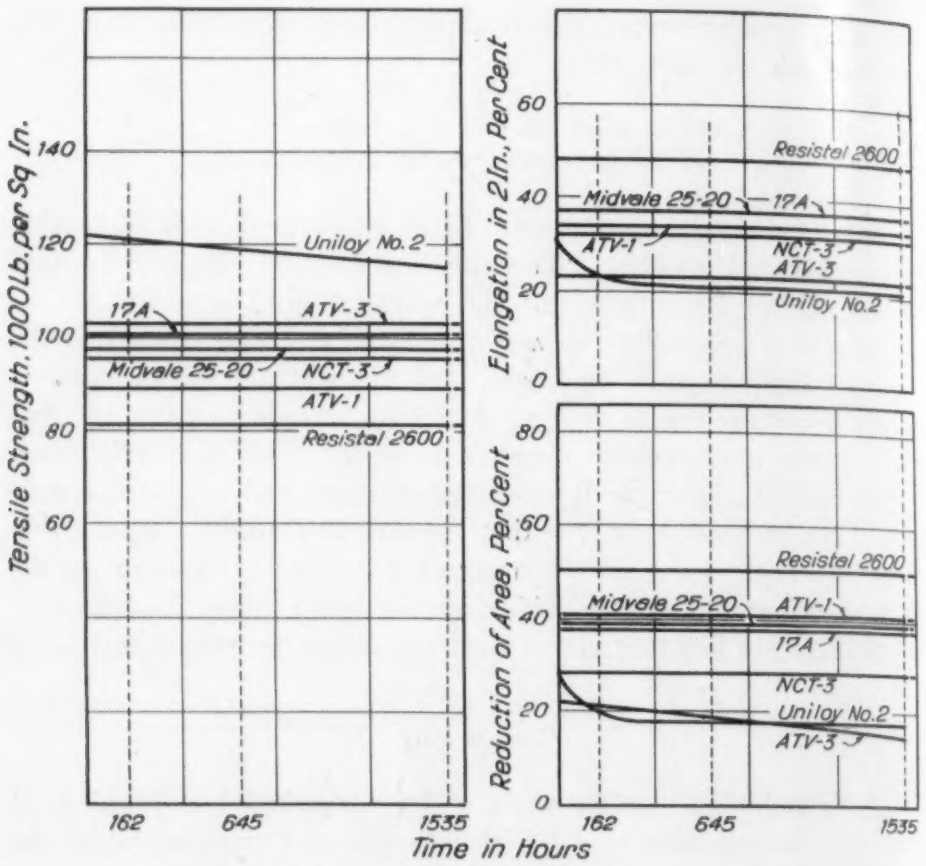

Fig. 3—Physical Properties of High Nickel-Chromium Ferrous Alloys.

J. L. Pearson, entitled, "The Trend of Progress in Great Britain on the Engineering Use of Metals at Elevated Temperatures."

In selecting metals for test under these process conditions there are several factors to be considered. In general, the carbon should be low, i.e., not over 0.40 per cent. The metal should be a single phase, or practically so. This will be difficult to attain if tungsten or molybdenum is used as an alloying element when the carbon 0.20 to 0.40 per cent is present, and the metal may require special heat treatment. Due to the fact that the service temperature will be one causing carbide precipitation in certain metals, care must be taken to select alloys that are reasonably resistant to carbide precipitation.

Experimental

Ten metals of high alloy content were selected for test. Bars of the specified size were made and exposed as described in the pre-

ceding sections. Three of the ten metals, while showing good physical properties, did not show consistent results, and accordingly will not be included in this discussion.

The seven metals that were used in these tests are as follows:

Metal	Approximate Composition
ATV-1	Cr 11; Ni 36; C 0.30
NCT,	Cr 25; Ni 20; Si 1, C 0.15
Midvale 25-20	Cr 25; Ni 20; C 0.18
ATV-3	Cr 14; Ni 26; W 3.5; C 0.4
Uniloy No. 2	Cr 21; Ni 12, Cu 1; Si 1.5; C 0.2
Rezistal 2600	Cr 8; Ni 22; Si 1.5; C 0.4
17A	Cr 8; Ni 20; C 0.4

The physical properties of the nickel-chromium-iron alloys are shown in Fig. 3.

Discussion of Results

The differences in the metal test bars after exposure were greater than might be expected from an examination of the curves. There were evidences of the beginning of surface attack on some which would have undoubtedly led to a break in the curve, if the test had been continued longer, which was impossible at the time. These results indicate that the majority of these metals are quite resistant to hydrogen-nitrogen attack. It is expected that the test period should be extended to 5000 hours in order to show distinguished differences between the better alloys in this group of seven.

Conclusion

No final conclusions have been reached with reference to the nickel-chromium-iron alloys. The work is unfinished and the present results are presented here only for the purpose of comparison with the results in the other two sections.

DISCUSSION

A. C. JONES:[1] Dr. Maxwell's offerings to technical gatherings are most interesting and illuminating and represent real work and conclusions carefully drawn. Unfortunately for me I have not had an opportunity of reading this paper and therefore may not properly discuss it. I am interested in his statement that the 18-8 type of alloy has not given satisfactory resistance to

[1]Metallurgist, Lebanon Steel Foundry, Lebanon, Pa.

the conditions involved in the process and would like to ask Dr. Maxwell if that was also true of modifications of 18-8, such as with 3 per cent molybdenum alloy low in carbon. (0.07 per cent max.)

DR. MAXWELL: It is to be expected that molybdenum modification of 18-8 as KA2 SMO would be better than the regular 18-8, but under the conditions of 500 degrees Cent. (930 degrees Fahr.), if any free carbides are present at all, it is going to cause trouble in this service. The small added expense of using a material of 25-20 or 25-12 Cr-Ni type will be found to be justified. The test bars that we used were of the size given in the paper, 1.5 x 0.5 x 12 inches. Most of them were cut from rolled plate, and were low carbon variety and heat treated.